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Arthur D. Little, Inc, Cambridge, Mass

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Industrial Environmental Research Lab, Research Triangle Park, N C

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Volume II. Laboratory and Pilot Plant Programs

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Program Report

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Volume II of the report covers Tasks I and II of a three-task program to investigate, characterize, and evaluate the basic process chemistry and the various operating modes of sodium-based dual alkali scrubbing processes. The tasks were: I, laboratory studies at both Arthur D. Little, Inc. (ADL) and IERL-RTP; II, pilot plant operations in a 1200 acfm system at ADL; and III, a prototype test program on a 20 MW dual alkali system at Plant Scholz. Dual alkali system operating modes on high and low sulfur fuel applications investigated included: concentrated and dilute dual alkali systems, lime and limestone regeneration, and slipstream sulfate treatment schemes. For each mode, the dual alkali process was characterized in terms of SO2 removal, chemical consumption, oxidation, sulfate precipitation and control, waste solids characteristics, and soluble solids losses.

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by

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ABSTRACT

This report presents the results of the Dual Alkali Program conducted by Arthur D. Little, Inc., (ADL) for the Industrial Environmental Research Laboratory, Research Triangle Park (IERL, RTP) of the U.S. Environmental Protection Agency (EPA). The purpose of the program was to investigate, characterize and evaluate the basic process chemistry and the various modes of operation of sodium-based dual alkali processes. The work was carried out at three levels of investigation:

- Task I – Laboratory studies at ADL and IERL, RTP.
- Task II – Pilot Plant Operations in a 1,200 scfm system at ADL.
- Task III – Prototype Test Program on a 20-megawatt Combustion Equipment Associates (CEA)/ADL dual alkali system at Plant Scholz, Southern Company Services, Inc./Gulf Power Company.

Various modes of operating dual alkali systems on high- and low-sulfur fuel applications were investigated, including:

- Concentrated and dilute sodium scrubbing systems
- Lime and limestone regeneration
- Slipstream sulfate treatment schemes.

In each mode, the objective was to characterize the dual alkali process in terms of SO_2 removal, chemical consumption, oxidation, sulfate precipitation and control, waste solids characteristics and soluble solids losses.

This is Volume II of the final report covering Tasks I and II, the laboratory and pilot plant programs. Volume I is the Executive Summary; Volume III covers the prototype test program, Task III.

VOLUME II

TASKS I AND II, LABORATORY AND PILOT PLANT PROGRAMS

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APPLICABLE CONVERSION FACTORS

ENGLISH TO METRIC UNITS

British	Metric
5/9 (°F-32)	°C
1 ft	0.3048 meter
1 ft²	0.0929 meters²
1 ft³	0.0283 meters³
1 grain	0.0648 gram
1 in.	2.54 centimeters
1 in²	6.452 centimeters²
1 in³	16.39 centimeters³
1 lb (avoir.)	0.4536 kilogram
1 ton (long)	1.0160 metric tons
1 ton (short)	0.9072 metric tons
1 gal	3.7853 liters
1 Btu	252 calories

I. SUMMARY

A. PURPOSE AND SCOPE

This report presents the results of the Dual Alkali Program conducted by Arthur D. Little, Inc., (ADL) for the Industrial Environmental Research Laboratory, Research Triangle Park (IERL, RTP) of the U.S. Environmental Protection Agency (EPA). The purpose of the program was to investigate, characterize, and evaluate the basic process chemistry and the various modes of operation of sodium-based dual alkali processes. The work covered a wide range of flue gas conditions, liquid reactant concentrations, and process configurations, including:

- concentrated and dilute mode (dilute sodium scrubbing solutions, active Na^+ concentration below about 0.15M)*
- use of lime and limestone for regeneration
- sulfuric acid treatment for sulfate control.

Each of the various modes was evaluated relative to the following performance characteristics:

- SO_2 removal capability
- oxidation and sulfate formation and control
- lime/limestone utilization
- waste solids properties
- sodium makeup requirements and degree of closed-loop operation
- process reliability.

Investigations were carried out at three levels: laboratory, pilot plant, and 20-megawatt prototype. Accordingly, the program was divided into three tasks:

- Task I -- Laboratory Program -- In the ADL laboratory program, experiments were performed on the regeneration of concentrated sodium scrubbing solutions using lime or limestone, and the use of sulfuric acid treatment for sulfate removal. Work also included characterization of the chemical and physical properties of dual alkali solids. Work was performed at IERL, Research Triangle Park on regeneration using limestone in dilute mode operation.

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*See Introduction and Glossary for dual alkali terminology.

- Task II -- Pilot Plant Program -- Pilot plant work was conducted at the Combustion Equipment Associates (CEA)/ADL pilot facility in Cambridge, Massachusetts. The following modes of operation were investigated in the pilot plant program:

  - concentrated mode using lime for regeneration

  - concentrated mode using lime for regeneration with slipstream sulfuric acid treatment for sulfate control

  - concentrated mode using limestone for regeneration

  - dilute mode using lime for regeneration.

- Task III -- Prototype Test Program -- The test program was conducted on the 20-megawatt CEA/ADL prototype dual alkali system at Gulf Power Company's Scholz Steam Plant in Sneads, Florida, from May 1975 to July 1976. The prototype system used lime in a concentrated mode. The system was operated on flue gas generated from moderately low- to high-sulfur coals, and with varying particulate loads to the system.

This is Volume II of the final report covering Tasks I and II of this program. Volume III covers the Prototype Test Program, Task III. An Executive Summary for the entire program has also been published as Volume I.

B. RESULTS AND CONCLUSIONS

Laboratory and pilot plant work on dilute and concentrated modes, using lime, indicates that these modes can be operated in a closed loop with the following general performance as a minimum:

- SO_2 removal -- 90% or greater.

- lime utilization -- 90% or greater.

- waste cakes solids content -- 45% or greater.

- sodium makeup requirements -- less than 0.05 mols Na_2CO_3/mol of SO_2 removed.

The actual performance of any particular dual alkali process will vary depending upon the SO_2 and oxygen concentrations in the flue gas, the design of the system and the concentration of sodium solutions used in the process. Using lime, some version of the dual alkali process can generally be designed to far exceed many or all of the above performance characteristics in most utility applications.

Aside from concentration differences, the principal difference in the operating characteristics between dilute and concentrated lime dual alkali systems is that dilute systems operate at or near saturation in calcium sulfate, potentially reducing the reliability and ease of operation of the dilute systems. Dilute systems require the use of carbonate makeup to provide some softening of the regenerated solution prior to recycle back to the scrubber.

No viable approach was developed in this program to enable the use of limestone for regeneration. The problem which remains to be solved is the production of solids with good settling characteristics over a wide range of sulfate, magnesium, and iron concentrations in the scrubbing liquor. These components tend to reduce the rate of reaction of limestone with sodium scrubbing solutions; solids properties tend to deteriorate with a decrease in the limestone reaction rate. However, these problems may be resolvable. There are considerable economic incentives for the substitution of limestone for lime in dual alkali processes, justifying further work in this area.

More specific results and conclusions regarding the various dual alkali modes and pilot plant operations are given below.

1. Pilot Plant SO_2 Removal and Oxidation - General

The pilot plant SO_2 removal and oxidation data are specific to the pilot plant scrubber configuration as influenced by the scrubber operating temperature for the pilot plant flue gas stream. The scrubber operating temperature of 140-150°F is higher than that normally encountered in conventional boiler flue gas applications (120-130°F). The elevated temperature in the pilot plant system tends to decrease SO_2 removal efficiency due to elevated SO_2 partial pressures for any given solution, and tends to increase oxidation rates. However, the purpose of the pilot plant scrubber and its operations was to provide scrubber effluent with an appropriate composition for use in the various dual alkali modes rather than to generate basic data on SO_2 absorption using sodium solutions.

Within the above constraints, the scrubber operations did indicate that SO_2 removal in excess of 90% is easily accomplished over a range of SO_2 inlet concentrations from 700-2,800 ppm by adjusting the scrubber feed stoichiometry. To achieve this removal efficiency, a stoichiometry of 1.1 mols of active Na^+ capacity/mol SO_2 inlet was required at the high inlet SO_2 range; a stoichiometry of 1.3 was required in the lower inlet SO_2 range. In any range of SO_2 concentration, increasing stoichiometry increased the SO_2 removal. There was no important apparent effect of active sodium concentration within a range of 0.2-0.5M or total dissolved solids concentration within a range of 5-15 wt %.

Sulfite oxidation is mass transfer limited at active sodium concentrations above 0.2M with the rate of oxidation increasing with the oxygen content of the flue gas. At lower active sodium concentrations the oxidation rate is roughly proportional to the active sodium concentration. The rate of oxidation decreases with increasing total dissolved solids; by increasing TDS from 6-15 wt % to 25-35 wt %, the oxidation rate is reduced by a factor of 2-3. At lower total dissolved solids in concentrated active sodium systems (0.3-0.6M active Na^+, 5-15 wt % TDS) sulfite oxidation can be expected to be on the order of 100-300 ppm equivalent SO_2 removal for oxygen concentrations in the flue gas ranging from 4 vol % to 8 vol %.

2. Concentrated Mode with Lime Regeneration

In the concentrated mode using lime for regeneration, calcium sulfate will coprecipitate with calcium sulfite at sulfate precipitation rates equivalent to oxidation rates as high as 25% of the SO_2 removal. Solutions remain unsaturated with respect to calcium sulfate and have low soluble calcium concentrations. Process modes can be operated over a wide range of sodium solution concentrations achieving high SO_2 removal (greater than 90%) producing good quality filter cake (45% solids, or greater) containing low soluble solids (2-5 wt % dry cake basis) with no sulfate purge required. The performance characteristics of concentrated lime regeneration modes are summarized in more detail below.

- SO_2 Removal -- SO_2 removal efficiencies in excess of 90% were easily achieved with the removal efficiency a function of sodium solution feed stoichiometry for any particular absorber design. In all closed-loop runs the feed stoichiometry (scrubber operating pH) was controlled to ensure better than 90% removal. For a given design, a slightly higher feed stoichiometry (or operating pH) was required for high sodium solution concentrations (30-35 wt % sodium salt solutions) than for moderate concentrations (10-15 wt % sodium salt solutions) to achieve the same removal efficiency because of the increase in SO_2 equilibrium partial pressure with the increase in sodium sulfite/bisulfite concentration.

- Lime Utilization -- Lime utilization in the range of 95-100% can be achieved with reactor holdup times of 35 minutes or greater when regenerating to a pH of 8 or higher. High utilizations can be achieved at shorter residence times if the regeneration reaction is not carried beyond neutralization of the bisulfite. Lime utilization decreases if regeneration is carried much beyond a pH of 12.5.

- Oxidation/Sulfate Control -- At active sodium concentrations above about 0.2M, calcium sulfate coprecipitates with calcium sulfite upon reaction of the sodium salt solution with lime. The sulfate/sulfite content of the precipitated calcium salts is related to the sulfate/sulfite concentrations in the reactor liquor by the following relationship:

$$\left(\frac{\text{mols } CaSO_4}{\text{mols } CaSO_3}\right)_{\substack{\text{reactor}\\\text{solids}}} = 0.0365\left(\frac{[SO_4^=]}{[SO_3^=]}\right)_{\substack{\text{reactor}\\\text{liquor}}} \quad (1)$$

This relationship describes the coprecipitation phenomenon over the range of sulfite and sulfate liquor concentrations used in laboratory and pilot plant experiments ($[SO_3] > 0.2M$, $[SO_4]/[SO_3] = 0 - 6$). This method of sulfate precipitation is effective for oxidation rates up to about 25%. At any given active sodium concentration, high sulfate precipitation appears to be favored by either partial neutralization of the absorbent solution or regeneration to pH's well above neutrality (> 11.5), thereby reducing the sulfite concentration in the reactor liquor and maximizing the sulfate/sulfite ratio in the liquor.

In a properly designed concentrated dual alkali loop, the sulfate/sulfite ratio will self-adjust at steady-state so that the rate of sulfate precipitation equals the rate of sulfite oxidation. It is possible to achieve this balance over a wide range of active sodium and sulfate concentrations in dynamic response to changes in flue gas rates and oxygen and SO_2 concentrations.

For dual alkali systems operating with high TDS (in the range of 25-30 wt % sodium salt solutions) oxidation rates can be reduced by a factor of 2-3 from those encountered at lowered TDS levels (10-15 wt %). At such high TDS levels, the active sodium concentrations as well as the sulfate concentration must be elevated in order to promote effective regeneration reactions and production of solids with acceptable dewatering properties. As a result, sulfate precipitation capability is limited.

- Solids Properties -- Single-stage CSTR (continuous stirred tank reactor) and multistage reactor systems can produce solids, over a wide range of process conditions, which settle well and filter to insoluble solids contents of 45 wt % or higher. When using a CSTR as the regeneration reactor, solids properties deteriorate as the regeneration reaction is carried to a higher pH range with the degree of deterioration increasing from pH 7.5 to pH 12. This effect is worse for reactor holdup times of 60 minutes than for shorter reactor residence times (30 minutes). Using a CSTR, solids properties also decrease as the sulfate/sulfite ratio increases in the reactor liquor (at higher oxidation rates). In a single-stage CSTR, it is difficult to produce solids with acceptable properties (45 wt % insoluble solids) at process conditions consistent with sulfate precipitation and sulfite oxidation rates much beyond 15%.

  Good quality solids can be produced over a wider range of pH and sulfate concentration using a two-stage reactor system, consisting of a short residence time reactor (5-10 minutes) followed in series by a longer residence time second stage (20-40 minutes). This multistage system produces good solids at pH levels up to about 12.5 and at sulfate/sulfite ratios required for sulfate precipitation rates equivalent to about 25% oxidation.

- Sodium Losses -- For a filter cake containing 50% insoluble solids, the soluble solids content of the cake can be reduced to 2-3% (dry cake basis) using the amount of filter cake wash water which would be normally available when operating closed-loop in a high-sulfur coal boiler application. At TDS levels in the range of 10-15 wt %, two to three displacement washes are effective in reducing the soluble content of the cake to 2-3 wt %. Of this material, 0.5-1.0 wt % soluble sodium salts appear to be occluded in the calcium salt crystals and cannot be washed regardless of the amount of wash water used. About two to three displacement washes are available for high-sulfur coal applications. At high TDS concentrations (30%), four to five displacement washes are necessary to reduce solubles to the 2-3% level. With only three displacement washes, solubles losses at high TDS concentrations can be expected to be roughly twice those expected when operating at 10-15 wt % TDS levels in the absorbent solution.

  At the lower TDS levels, sodium makeup requirements are on the order of 2-3% of the total alkali requirement (mol basis). That is, roughly 2-3% of the sulfur absorbed from the flue gas leaves the system as sodium salts with the remainder as calcium salts.

  From the above considerations, operating a concentrated lime mode with TDS in the range of 10-15%, the single-stage CSTR can produce good quality solids (45 wt % or greater) containing 2-3 wt % solubles at system oxidation rates up to 15%. When using the multistage reactor system the operability of the process is extended to oxidation levels in the range of about 25%. Increasing TDS reduces oxidation but requires more wash water to produce the same cake solubles content. At two to three displacement washes, the solubles content of the cake is proportional to the TDS levels in the system loop.

- System Operability/Reliability -- In concentrated modes using lime for regeneration, soluble calcium concentrations range from 15-90 ppm with the calcium concentration generally decreasing with increasing sulfite concentration. No scaling or deposition of solids was observed in the scrubber loop during any of the concentrated mode operations. Scrubber operation and SO_2 removal were easy to control. The regeneration reaction is stable and easy to control, but should be kept at a pH below about 8 if operating with a single-stage regeneration reactor. Increasing the TDS level in the system raises the sodium salt saturation temperature, increasing the potential for solid sodium salt crystallization in elements of the system which are permitted to cool.

1. Concentrated Mode with Sulfuric Acid Sulfate Treatment

The sulfuric acid slipstream treatment scheme is a technically feasible and reliable approach for removal of soluble sulfates from dual alkali systems. The basic chemistry of the treatment process is given in the following simplified reaction equation:

$$2CaSO_3 \cdot 1/2H_2O(\text{filter cake}) + Na_2SO_4(\text{system liquor}) + H_2SO_4 + 3H_2O \rightarrow 2NaHSO_3 + 2CaSO_4 \cdot 2H_2O \qquad (2)$$

The treatment produces sulfate in the form of gypsum that can be readily dewatered to 65 wt % insoluble solids or higher. The scheme adds complexity to any dual alkali mode to which it is applied. The complexity is reflected in additional capital costs and in increased operating costs for the sulfuric acid, the additional lime consumed and the additional solid waste produced.

The amount of sulfuric acid required is important since it directly affects the overall lime requirement. As the sulfuric acid addition rate increases, the lime rate must increase accordingly for precipitation of the additional sulfur value added to the system. The maximum efficiency of the treatment scheme ((mols Na_2SO_4 removed/mol H_2SO_4 fed) x 100%) appears to be practically limited to a maximum in the range of 60-70%. In order to precipitate sulfate at a rate sufficient to keep up with an oxidation rate of 15% (of the SO_2 absorbed), the lime feed requirement will be increased by 25% for a 60% reactor efficiency.

The efficiency of the sulfuric acid treatment is importantly affected by the calcium utilization achieved in the absorbent regeneration reactor in the main dual alkali loop. As calcium utilization decreases in the main loop the efficiency of the sulfuric acid slipstream treatment decreases and acid consumption increases to neutralize unreacted lime in the filter cake. In order to achieve a 50% efficiency in the sulfuric acid treatment system, calcium utilization in the main dual alkali loop must exceed 90%.

Because the use of this sulfuric acid treatment scheme may be costly when applied to systems with high oxidation rates (due to the sulfuric acid and extra lime requirements), it may be more appropriate for systems with intermediate levels of oxidation where the rate of sulfate formation cannot be easily handled in a simpler concentrated sodium mode. The consequences of using the sulfuric acid slipstream treatment approach for sulfate regeneration should, therefore, be carefully evaluated in terms of the overall process operation. In many cases, where oxidation rates are high enough that they cannot be easily handled by normal concentrated mode operation, other dual alkali approaches, such as the dilute lime system described in Chapter VII, might be more promising than a sulfuric acid treatment scheme.

4. Concentrated Mode with Limestone Regeneration

No viable approach was found for use of limestone in a concentrated dual alkali mode. Through the laboratory and pilot plant efforts allocated to work on the concentrated limestone mode, we were not able to develop process parameters and reactor conditions consistent with good limestone utilization and generation of an acceptable quality of waste solids. The work did, however, uncover important factors influencing the limestone regeneration reaction that indicated promising areas of future work. Unlike results from work on use of limestone in dilute modes (Chapter VII), the potential for technical success argues for additional work on the concentrated limestone dual alkali mode, especially when the economic incentives (presented in Chapter II) are considered.

Limestone is substantially less reactive toward sodium salt solutions than is lime, even wher reacting with relatively acidic scrubber bleed solutions. The reaction rate of the limestone regeneration reaction is dependent upon:

- nature of the limestone and its particle size;
- reactor temperature and residence time;
- concentrations of soluble reactants (sodium sulfites, sodium bisulfites and sodium sulfates); and
- the presence, at low concentrations, of trace constituents such as magnesium and iron, which influence the reaction rate.

Increase in the reaction rate was generally consistent with improvement in the dewatering properties of the solids produced and with improved utilization of limestone.

Three limestones, with similar particle size distribution, were examined -- Fredonia limestone used in the EPA/TVA Shawnee program; another, locally available, natural limestone; and reagent grade $CaCO_3$. Of these, the Fredonia limestone was amorphous, rather than crystalline in nature, and was considerably more reactive than the other two limestones examined. The Fredonia limestone, therefore, was used extensively in the laboratory and pilot plant programs.

Laboratory experiments indicated that increasing temperature importantly increased the reaction rate. However, the pilot plant was not equipped for heating the reactors or for heating the reactor feed. As a consequrnce pilot plant regeneration was performed at a maximum of about 50°C.

The dewatering properties of solids were generally observed to deteriorate as the regeneration reactor residence time was increased. Increasing the reactor residence time results in carrying out the reaction closer to the equilibrium conditions and consequently at a lower driving force and reaction rate. Use of multistage reactor systems, containing several stages with residence times in the range of 15 minutes, were found to produce solids with a quality superior to that of solids produced in fewer reactors with the same total residence time. Recycle of solids, increasing reactor solids concentrations from about 2 wt % to 5 wt %, improved limestone utilization but did not appreciably improve the quality of the solids.

Under controlled conditions, with a multistage reactor system operating at about 50°C, it was possible to produce solids with acceptable dewatering properties (65% insoluble solids) and to achieve limestone utilizations on the order of 75%. However, as the sulfate concentration in the loop rose above 0.7M, or, the magnesium concentration rose much above 300 ppm, the reaction rate and the resulting limestone utilization and solids properties all deteriorated.

Sulfate concentration in the reactor liquor had a much more important, deleterious effect on the reaction rate and solids properties in limestone regeneration reactions than the similar effects of increased sulfate concentration observed in concentrated lime regeneration. As in lime regeneration, the reaction rate is inversely proportional to the ratio of sulfate/sulfite concentrations in the liquor; but the rate drops dramatically using limestone as the sulfate concentration exceeds 0.7M at TOS levels of 0.3-0.5M. Operation at lower sulfate/sulfite ratios tends to limit sulfate precipitation in this mode and limit the range of oxidation in which limestone regeneration could be operated closed-loop.

Calcium sulfate coprecipitates along with calcium sulfite in concentrated limestone regeneration reactions in an analogous fashion to the coprecipitation of calcium sulfate observed in the concentrated lime regeneration. However, pilot plant data indicate that for the same sulfate/sulfite concentrations with the same range of TOS in the feed liquor (i.e., [TOS] = 0.3-0.5M), lower sulfate precipitation occurs when using limestone, as given by the following:

$$\left(\frac{CaSO_4}{CaSO_3}\right)_{\substack{\text{reactor}\\\text{solids}}} = 0.022\left(\frac{[SO_4^=]}{[SO_3^=]}\right)_{\substack{\text{reactor}\\\text{liquor}}} \qquad (3)$$

The sensitivity of the reaction to high sulfate concentrations and the lower sulfate precipitation rates make limestone regeneration less viable for closed-loop operation than lime regeneration at higher oxidation rates.

The presence of Mg^{++} in solution, introduced into the system in varying amounts depending upon the magnesium content of the limestone, also can have a retarding effect on the limestone regeneration reaction rate, resulting in poor solids quality and limestone utilization. This effect becomes pronounced as the Mg^{++} concentration rises much above a few hundred ppm. Relatively low magnesium limestones, such as Fredonia limestone (1.0-1.5 wt % Mg as $MgCO_3$) would result in concentrations on the order of a few thousand ppm, at steady-state, in a concentrated dual alkali loop.

Laboratory work confirmed that magnesium concentrations could be controlled by reacting part of the process stream with lime to precipitate $Mg(OH)_2$. However, such an approach would reduce operating cost savings, requiring part of the total regeneration to be performed using lime. Use of lime with limestone would increase the complexity and the capital cost in a manner similar to that discussed in Chapter VI for dilute limestone/lime dual alkali systems, eliminating economic incentives.

In pilot plant operations, iron from corrosion of unlined steel equipment was found to have an effect similar to that of magnesium on the limestone regeneration reaction at pH's below about 6. At higher pH's, $Fe(OH)_3$ is highly insoluble, limiting the buildup of iron in solution. By selection of proper materials of construction and linings and by carrying the limestone regeneration beyond a pH of 6, interference by iron can be eliminated in concentrated limestone modes.

Future work on limestone regeneration should be directed at increasing reaction rates at high magnesium levels by increasing sulfite concentrations, reactor temperature and by staging of the reactors.

5. Dilute Mode with Lime and Limestone Regeneration

Use of limestone only for the regeneration of solutions in the dilute mode (less than 0.15M active sodium) is not viable. The limestone reaction rate decreases as the ratio of soluble sulfate/sulfite increases in the reactor solutions. At sulfate/sulfite ratios required for adequate sulfate precipitation in the dilute mode, reaction rates are poor and result in poor limestone utilization and poor solids quality.

Use of lime in combination with limestone in a dilute dual alkali mode was more viable technically. In this approach, the lime regeneration was carried out in a second reaction system to promote sulfate precipitation. The limestone/lime process is more complicated than a simple dilute lime process, resulting in higher projected capital cost. Economic analysis indicated that operating cost savings which could potentially be realized in using limestone for part of the regeneration would not offset the additional capital cost probably required to enable use of the limestone. The dilute lime system, using soda ash for softening, was technically and economically the most viable dilute mode considered. Conclusions based upon laboratory and pilot plant investigations of this mode are given below.

A dilute lime mode can be operated in a closed loop with sulfate precipitation keeping up with any level of system oxidation. The system can be operated with high SO_2 removal (90% or higher) and good lime utilization (90% or higher) to produce high quality solids (60% insolubles or higher) with low soluble sodium losses (2% achievable). The process may be more appropriate for low-sulfur coal applications or in situations where oxidation rates are expected to exceed 25-30% of the SO_2 removal. The dilute lime mode is somewhat more complicated than the concentrated lime mode, involving higher liquid rates and larger reactors and associated equipment. The process is also potentially less reliable than the concentrated lime approach.

The regeneration reaction, carried out at low sulfite levels, results in the precipitation of calcium sulfate (usually gypsum) to produce a regenerated solution of sodium hydroxide and sodium sulfate with soluble calcium levels which are, at best, at the saturation level of about 700 ppm Ca^{++}. Even with moderate amounts of soda ash makeup (and resulting softening by precipitation of calcium carbonate) the solutions have soluble calcium levels in the range of 600-700 ppm with a high potential for scaling in the system. Close control of scrubber pH is required to prevent carbonate or sulfite scaling. High scrubber oxidation rates may create sulfate scaling.

In the dilute mode regeneration reaction, there is a high tendency to produce solutions which are supersaturated in Ca^{++} (with respect to gypsum). Using a single-stage CSTR with no solids recycle, calcium supersaturation levels of 100-200 ppm are easily achieved. Special design precautions must be taken to prevent supersaturation and the resulting scaling throughout the system. Supersaturation can be reduced in a number of ways, by reactor system design and by controlling conditions of the regeneration reaction:

- Increased reactor residence time -- Allows time for completion of reaction and desupersaturation. Holdup time of 60 minutes is a minimum; 90 minutes is preferable.

- Solids recycle -- Increases suspended solids concentration and seed concentration for reaction and desupersaturation. Recycle of solids to achieve a concentration of 4% or higher suspended calcium salt solids is required to eliminate supersaturation in the reactor effluent.

- Oxidation of sulfite in scrubber bleed prior to regeneration -- Lowers the concentration of TOS which tends to retard the lime/sulfate reaction when TOS is present in the dilute mode concentration range. Oxidation to TOS concentrations of about 0.02M or lower is desirable.

- Multistage reactor configuration -- Solids generated in a short residence time first stage provide good seeds for completion of reaction in longer residence second stage. Using a multistage reactor can reduce supersaturation to within about 50 ppm of the saturation level. Solids recycle is required to completely eliminate supersaturation.

Elimination of supersaturation was achieved in the single-stage reactor, with 90 minutes residence time; using solids recycle to the minimum of 4% suspended calcium salts in the reactor; and with oxidation of the reactor feed solution to TOS levels of 0.02M or lower. Variation in soluble sulfate concentrations in the range of 0.50-0.75M had no apparent effect on the level of supersaturation.

Utilizing these design factors in a dilute mode with lime regeneration not only reduces or eliminates supersaturation, but also promotes a good reaction rate which generally improves the overall process performance parameters such as lime utilization, sulfate precipitation and solids properties. More specifically, the performance of the dilute lime mode relative to the important process performance characteristics is given below:

- SO_2 removal -- SO_2 removal of 90% is easily achieved especially at low to medium inlet SO_2 levels. SO_2 removal is not as efficient as in a concentrated dual alkali mode (with the same scrubber configuration) because of the low active sodium concentration. The scrubber operation is more difficult to control due to the low buffering capacity of the dilute mode liquors. Higher calcium concentrations (in the range of 600-700 ppm Ca^{++}) present potential scaling problems in the scrubbing system. Operation of the scrubber in a high pH range (9-11) to promote good SO_2 removal results in some CO_2 absorption and potential carbonate scale formation. Increasing active sodium concentrations to provide more buffering can result in sulfite scale formation in the pH range of 8-11.

- Lime utilization -- Lime utilization of 90% or higher is achievable when regenerating to hydroxide concentrations of about 0.1M with solutions containing sulfate in the range of 0.50-0.75M and using reactors with a minimum total holdup time of 60 minutes. Utilization increases as the residence time and sulfate concentration are increased. Solids recycle also helps increase lime utilization. However, TOS levels in the feed to the reactor should be 0.02M or less (by deliberate oxidation if necessary) to prevent retarding of the reaction rate by the sulfite.

- Oxidation/sulfate control -- Complete sulfate control is possible in this mode of operation at any rate of oxidation in the system. However, at very high scrubber oxidation rates, sulfite/bisulfite buffering is minimal and scrubber pH control becomes difficult. All other aspects of the process operation are improved by high oxidation rates (i.e., minimal TOS concentration in the feed to the regeneration reactor). Deliberate oxidation should be used to maintain TOS levels below about 0.02M. At sulfate concentrations in the range of 0.50-0.75M, calcium sulfate (usually gypsum) is produced instead of a mixed calcium sulfite/calcium sulfate crystal, when TOS is maintained at or below 0.02M. At this point the calcium sulfate content of the solids is no longer limited by the apparent maximum content of 25-30% in the mixed crystal; 100% calcium sulfate can be produced.

- Solids properties -- It is possible to produce excellent quality solids containing 60-80% insoluble solids. Good solids properties are favored by the following conditions:

  - Low TOS in the reactor feed -- less than 0.02M.

  - High sulfate in the reactor feed -- 0.50-0.75M (high end of range favored).

  - Solids recycle -- improves solids quality but increases the solids load and ultimately the size of the thickener.
  - Multistage reactor system -- improves solids quality compared to same total residence time in a single stage.
  - High reactor residence time -- 90% insoluble solids can be produced using a 90 minute residence time reactor.

- Sodium losses -- In any application, increasing the insoluble solids content of the filter cake increases the effective number of displacement washes for any given amount of wash water available. By producing 75% insoluble solids in a high-sulfur coal application, roughly five displacement washes are available (as opposed to two and one-half displacement washes at 50% solids) permitting more effective cake washing; in low-sulfur coal applications even more wash water can be available. Consequently, sufficient wash water should be available to reduce the solubles content of the cake to under 2%; and down to the range of 0.5-1.5% solubles in low-sulfur coal applications. In such applications it may be possible to wash the filter cake to loss levels lower than those corresponding to sodium carbonate makeup levels required for softening of the regenerated liquor. A sodium carbonate makeup rate of 2.0-2.5% of the SO_2 removal rate provides sufficient carbonate to reduce the Ca^{++} concentration in the regenerated liquor by about 50 ppm, providing only minimum softening. Thus, sodium makeup (and ultimately the losses in the cake) may be controlled by softening requirements rather than by wash water availability or cake washability.

- System operability/reliability -- The dilute lime mode is inherently less reliable and more difficult to control than the concentrated lime mode. When appropriate care is taken to eliminate supersaturation, the calcium levels in the regenerated solution are in the range of 700 ppm. Only a minimum of softening is provided at low sodium carbonate makeup levels. Potential for scaling exists in the reactor system and associated auxiliaries and piping, and in the absorber. Absorber operation is less effective and more difficult to control than in the concentrated mode.

6. Solids Characterization -- Dilute and Concentrated Lime Regeneration Modes

Limited testing was performed to characterize the basic physical and chemical properties of ash-free waste filter cakes produced in the two most successful dual alkali modes piloted -- concentrated and dilute active sodium modes with lime regeneration. Testing included: analysis of major chemical constituents; crystalline morphology via X-ray diffraction and scanning electron microscopy; unconfined compressive strength and optimum dry density; permeability; leaching behavior; and the effects of treatment with lime (or portland cement) and fly ash on the physical properties.

The concentrated mode filter cake that was tested was produced in the prototype system using the two-stage reactor. The cake was a mixture of calcium sulfite and sulfate (about 15% calcium sulfate) and contained 55% solids. The crystalline structure of the solids was rosette-like agglomerates of needles characteristic of the concentrated mode operation. X-ray diffraction data and chemical analyses indicate that the calcium sulfite and calcium sulfate were coprecipitated as a mixed crystal of hemihydrate salts. There was no evidence of gypsum ($CaSO_4 \cdot 2H_2O$) in the solids.

The dilute mode filter cake was essentially pure gypsum produced in the pilot plant under conditions of intentional oxidation. The solids crystals were monoclinic and the filter cake contained approximately 80% insoluble solids.

The mixed sulfite/sulfate solids had the appearance and physical properties similar to a silt-like soil and handled much like a moist powder. The gypsum, on the other hand, was much more grainy and had the consistency of a sandy soil. The unconfined compressive strengths of both materials were in the range of typical soils, 10-15 psi; and both had optimum dry densities in the range of 75% solids. The coefficient of the permeability of the compacted sulfite/sulfate solids ranged from about 3×10^{-6} to 5×10^{-5} cm/second. The permeability of dual alkali gypsum was 2×10^{-5} cm/second. These values are within the range of published data on coefficients of permeability of gypsum and sulfite-rich solids produced in FGD systems.[1,2]

The treatment of the sulfite/sulfate filter cake was studied using various mixtures of lime (or portland cement), filter cake, and fly ash. This work showed that the concentrated mode solids could be treated in a fashion similar to the treatment of solids from direct lime and limestone scrubbing systems with similar effects on the mechanical properties. Testing performed on prototype system concentrated dual alkali solids by IU Conversion Systems (IUCS) indicates that the coefficient of permeability of treated filter cake was about 5×10^{-6} cm/second using standard treatment mixes.[2]

Accelerated leaching tests and elutriate analyses performed on untreated samples both at ADL and by IUCS showed that the initial and "steady-state" concentrations of soluble species that can be leached, notably total dissolved solids (TDS) and total oxidizable sulfur (TOS), will be very dependent upon the initial conditions and composition of the solids (degree of cake washing, ratio of sulfate-to-sulfite, chloride concentration in the gas, etc.) and the manner of solids handling and disposal. TDS levels in the initial leachate can range from a few thousand ppm to about ten thousand ppm, and "steady-state" concentrations (after the first few pore volume displacements) can vary from a few hundred ppm to approximately a thousand ppm. Similarly, TOS levels can range from essentially nil to up to 50 ppm. These concentrations are consistent with the range of published data for leachates from solids generated in direct lime and limestone scrubbing systems.

Testing performed by IUCS on the treatment of the filter cake indicated significant reductions in both initial and "steady-state" levels of TDS in leachates. Depending upon the type of treatment, reductions of 50% to 80% were observed.

In all physical properties testing performed at ADL, samples were prepared in accordance with standard soil-mechanics testing procedures. These procedures required, as a part of the sample preparation, the drying and rewetting of the filter cake to achieve a desired solids content. While the samples were dried at temperatures of 83°C to prevent loss of water of hydration, there is still concern that the drying/rewetting procedure resulted in some changes in the behavior of the material, particularly in the case of the rosette-like crystals produced in the concentrated mode operation. However, the results of these limited tests are believed to be indicative of the general behavior of the dual alkali solids. More exhaustive testing on both as-received samples and samples prepared in accordance with standard soil testing procedures is required to assess the effects of sample preparation on test results.

II. INTRODUCTION

A. BACKGROUND AND OBJECTIVES

Dual alkali or double alkali are generic terms used to describe flue gas desulfurization (FGD) processes involving absorption of SO_2 using a soluble alkali, followed by reaction of the scrubber effluent solution with lime and/or limestone, to produce a solid calcium sulfite/sulfate salt and to regenerate the soluble alkali scrubber feed solution. Many versions of dual alkali processes are under development. Most of the advanced systems utilize sodium as the soluble alkali, but ammonia-based and other systems also are receiving development effort. In addition to the type of soluble alkali used, another important difference among the dual alkali processes is the concentration of soluble alkali in the absorption/regeneration loop. The concentration and the choice of soluble alkali are importantly related to the reactions involving soluble sulfate produced in the system and to the control of soluble solids losses from the system. Many of the various schemes for dual alkali processes and the general chemistry and technology have been reviewed by Kaplan at a recent EPA FGD Symposium.[3] A glossary of dual alkali terminology is included in this report.

Work in the EPA/ADL Dual Alkali Program was limited to sodium-based dual alkali systems, covering a wide range of active sodium concentrations using lime and/or limestone for regeneration. Special attention was given to the formation and precipitation of sulfate and to the control of the soluble solids content of the calcium salts which are produced for disposal.

The objectives of the EPA/ADL Dual Alkali Program were to define promising sodium-based dual alkali modes of operation and characterize those modes with regard to SO_2 removal, yields on reactants, sulfite oxidation, sulfate precipitation, waste solids characteristics, soluble solids losses, and overall process reliability.

The program was divided into three task areas as follows:

- Task I
    - ADL Laboratory Studies -- Performed at ADL laboratories, Cambridge, Massachusetts -- Regeneration of concentrated sodium scrubbing solutions using lime regeneration, limestone regeneration, sulfuric acid treatment for sulfate removal, detailed characterization of the physical and chemical properties of solids produced in these regeneration modes.
    - EPA Laboratory Studies -- Performed at EPA's Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina -- Regeneration of dilute sodium scrubbing solutions using lime regeneration, limestone regeneration and lime/limestone regeneration.

- Task II

  - ADL Pilot Plant Studies -- Performed at CEA/ADL Pilot Facility, Cambridge, Massachusetts -- Promising modes of operation using dilute and concentrated sodium scrubbing solutions with lime regeneration, limestone regeneration, and sulfuric acid treatment for sulfate precipitation.

- Task III

  - Test Program -- Performed at the prototype dual alkali system, Plant Scholz, Gulf Power Company/Southern Company Services, Inc. -- Lime regeneration of concentrated sodium scrubbing solutions using the 20-megawatt CEA/ADL system.

Consistent with the program objectives, the important process characteristics were determined for each of the dual alkali modes investigated in each task.

B. DESCRIPTION OF CHEMISTRY AND DEFINITION OF TERMS

In the absorption section of sodium-based dual alkali processes, absorption of SO_2 in sodium sulfite solutions occurs to produce a bisulfite scrubber effluent solution according to the overall reaction:

$$Na_2SO_3 + SO_2 + H_2O \rightleftarrows 2NaHSO_3 \qquad (4)$$

Depending upon the dual alkali mode being used, the feed to the absorber may also contain some sodium hydroxide (formed in the regeneration section or used as sodium makeup) and/or sodium carbonate (used as sodium makeup to the system). Both sodium carbonate and hydroxide form sodium sulfite on absorption of SO_2:

$$Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2 \qquad (5)$$

$$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O \qquad (6)$$

which is used in further absorption to produce bisulfite. The absorber feed solution will also contain some level of sodium sulfate in solution and may contain some sodium bisulfite if neutralization is not completed in the regeneration section. Sodium, identified as associated with anions involved in SO_2 absorption reactions, is referred to as "active" sodium (includes sodium sulfite, bisulfite, hydroxide and carbonate/bicarbonate). The sulfite/bisulfite content of solutions, or total oxidizable sulfur content, is also referred to as TOS.

Some oxidation of sulfite to sulfate occurs in the absorber due to reaction of sulfite with oxygen in the flue gas:

$$2Na_2SO_3 + O_2 \rightleftarrows 2Na_2SO_4 \qquad (7)$$

The rate of oxidation or oxygen transfer in the absorber is a function of the absorber design, oxygen concentration in the flue gas, flue gas temperature, and the nature and concentration of the species in the scrubbing solution. For a given set of process parameters, the oxidation rate in mols of sulfite oxidized per unit time is relatively independent of the SO_2 removal rate. The oxidation rate can be expressed, on an equivalent basis, as a percentage of the SO_2 removed. As an example, for a high-sulfur utility boiler flue gas containing about 4-5% O_2, at about 2,500 ppm SO_2 removal, approximately 10% of the SO_2 removed from the flue gas will show as sulfate in the scrubbing solution and the remaining 90% will show as sulfite/bisulfite. At steady state, this sulfate make, equivalent to 10% of the SO_2 removed, must leave the system, either as calcium sulfate or as a purge of sodium sulfate, at the rate at which it is being formed in the system.

Under similar conditions of absorber design, oxygen concentration and solution characteristics, but at a much lower SO_2 removal rate (as in a low-sulfur coal application), a similar rate of oxygen absorption/reaction will result in a much higher equivalent percentage of the SO_2 removed -- perhaps as high as 50% of the SO_2 removed. Also, in industrial boiler applications, where operation at higher excess air often occurs, high equivalent oxidation rates can be encountered even in high-sulfur coal applications. As a consequence, in order to avoid unacceptable sodium sulfate purge requirements from dual alkali systems, modes of operation capable of precipitating both sulfite and sulfate are required; the sulfate and sulfite must leave the system as solid calcium salts with sodium sulfate and sodium sulfite losses minimized.

The regeneration of acid sodium sulfite/sulfate scrubber effluent solutions can be considered as a sequential reaction first involving neutralization of the bisulfite using either lime or limestone, to produce a precipitute of calcium sulfite:

$$2NaHSO_3 + Ca(OH)_2 \rightarrow Na_2SO_3 + CaSO_3 + 2H_2O \qquad (8)$$

$$2NaHSO_3 + CaCO_3 \rightleftarrows Na_2SO_3 + CaSO_3 + CO_2\uparrow + H_2O \qquad (9)$$

In theory, the lime neutralization reaction should go to completion; complete neutralization of bisulfite is not possible with $CaCO_3$. Using lime, the regeneration can be carried beyond neutralization to generate caustic

$$Na_2SO_3 + Ca(OH)_2 \rightleftarrows 2NaOH + CaSO_3 \qquad (10)$$

to some equilibrium hydroxide concentration. The usual form of calcium sulfite produced is the hemihydrate, $CaSO_3 \cdot 1/2H_2O$.

Depending upon the concentration of sulfite and sulfate and the pH of the solution, the following reaction for sulfate removal also occurs simultaneously with neutralization and regeneration reactions (8) - (10) using either lime or limestone:

$$Ca^{++} + SO_4^{=} \rightleftarrows CaSO_4 \qquad (11)$$

The form of this calcium sulfate was investigated and will be discussed later in this report.

Thus, the level of sulfate precipitation in the overall scheme is given by the ratio of calcium sulfate to total calcium/sulfur salts produced:

$$\text{Sulfate Precipitation} = \frac{\text{mole } CaSO_4}{\text{mole } CaSO_4 + \text{ mole } CaSO_3}$$

If the level of sulfate formation or sulfite oxidation given by:

$$\text{Sulfate Formation} = \frac{\text{mole } SO_3^= \text{ oxidized}}{\text{mole } SO_2 \text{ removed}}$$

is matched by the level of sulfate precipitation, then all sulfur removed from the flue gas can leave the system as a calcium salt and no soluble sulfate purge is necessary to maintain a sulfate balance in the system. In practice, even if such a balance is established, the washed calcium sulfite/sulfate salts will contain some soluble sodium salts as well as soluble fly ash constituents which must be purged and some sodium makeup to the system will therefore be required. Calcium utilization or yield in the overall process is defined as:

$$\text{Calcium Utilization} = \frac{(\text{mole } CaSO_3 + \text{ mole } CaSO_4) \text{ generated}}{\text{mole Ca fed}} \times 100\%$$

regardless of whether lime or limestone is used.

Dual alkali modes can be designed to accommodate varying levels of oxidation, with equivalent precipitation, up to an oxidation rate of 100%. For example, in the limit, a solution of about 0.5 molar sodium sulfate can be reacted with lime according to the following equation:

$$Na_2SO_4 + Ca(OH)_2 + 2H_2O \rightleftarrows 2NaOH + CaSO_4 \cdot 2H_2O \qquad (12)$$

to produce gypsum and a solution containing approximately 0.10-0.15 molar sodium hydroxide and 0.43 molar sodium sulfate. If this solution, containing this relatively dilute concentration of active alkali, is recycled to the absorber where 100% oxidation occurs, then a 0.5 molar sodium sulfate solution is returned to the regeneration system and the cycle is repeated. A dual alkali system can be designed on this basis.

As the sulfite concentration in the scrubber effluent is increased, increasing the sulfite/sulfate concentration ratio in solution, the percent sulfate precipitation decreases. However, the higher concentration of active sodium species (sulfites, hydroxide and carbonates) reduces both the scrubber liquid feed rate requirement and the feed rate to the regeneration system, for a given SO_2 removal rate. As the concentration of active sodium increases, the regeneration system size is thereby reduced as are the liquid rates throughout the system. Thus, as the sulfate precipitation requirements decrease, the system size and recirculation rates can be reduced by increasing active sodium concentrations.

Regeneration reactions in the "concentrated mode" produce solutions saturated (or possibly supersaturated) with respect to calcium sulfite; in the "dilute mode" saturation (or possibly supersaturation) is with respect to calcium sulfate (gypsum). For purposes of this program, dilute operating modes are considered to be those involving solutions containing active sodium concentrations less than or equal to 0.15 molar active Na^+, where active sodium is sodium sulfite/bisulfite, carbonate/bicarbonate or hydroxide. Concentrated modes are those involving solutions containing active sodium concentrations greater than 0.15 molar active Na^+. Soluble calcium levels in dilute mode regenerated solutions are quite high compared to levels in the concentrated mode, usually requiring "softening" with carbonate

$$Ca^{++} + CO_3^{=} \rightleftarrows CaCO_3 \qquad (11)$$

to prevent scaling by precipitation of calcium salts in the scrubber.

In the absorption of SO_2 with a regenerated solution, a reduction in pH occurs, converting $SO_3^{=}$ to HSO_3^{-}, thereby increasing the Ca^{++} solubility relative to $CaSO_3$ due to the reduction in $SO_3^{=}$ concentration. Therefore, the solution becomes less saturated relative to $CaSO_3$ as the pH drops below about 9. A similar reduction in saturation relative to $CaSO_4$ does not occur until the pH is reduced below about 3, where conversion of $SO_4^{=}$ to HSO_4^{-} begins to become significant. Scrubbers for sodium dual alkali systems are generally designed to operate above a pH of 5. Thus, dilute solutions, saturated (or supersaturated) with $CaSO_4$ do not benefit from the pH reduction for prevention of scale in the scrubber.

As will be discussed in more detail, the sulfite and sulfate concentrations, besides affecting sulfate precipitation, also have a profound effect on the physical properties of the calcium/sulfur salts. As a result, the settling and filtration characteristics of the solids produced in dual alkali modes are also affected.

As an alternate approach to operating at decreased active sodium concentrations, high levels of sulfate precipitation can be achieved using sulfuric acid treatment for precipitation of sulfate according to the following equation:

$$Na_2SO_4 + H_2SO_4 + 2CaSO_3 \cdot 1/2H_2O + 3H_2O \rightleftarrows 2NaHSO_3 + 2CaSO_4 \cdot 2H_2O \qquad (2)$$

This reaction is carried out at a low pH (2-3), where sulfite is converted to bisulfite, thereby bringing calcium sulfite into solution and exceeding the solubility product for calcium sulfate. This reaction can be applied on a process slipstream for sulfate precipitation, as required. However, in the overall process this scheme utilizes sulfuric acid, requiring additional lime or limestone for ultimate neutralization of this acidity added to the system and generates an equivalent additional amount of waste calcium/sulfur salts. This scheme is being practiced commercially in Japan and offers the advantage of operating a concentrated active sodium absorption/regeneration system with the ability to sustain high sulfate oxidation levels with equivalent precipitation of calcium sulfate.

The use of limestone rather than lime in the dual alkali process has important economic incentives, especially for high-sulfur coal applications. For a typical application:

- Coal = 3.5% S; 12,000 Btu/lb
- Load Factor = 80%
- Heat Rate = 10,000 Btu/kwh
- Lime = \$40/ton CaO; 95% utilization
- Limestone = \$5/ton $CaCO_3$; 85% utilization
- Waste Disposal = \$10/ton dry

at 90% SO_2 removal, operating costs for the lime-based dual alkali system are 6.8¢/MMBtu higher than if using limestone. At a total fixed cost of 20%/year of the capital investment (including maintenance), the operating cost savings with limestone would support an additional capital investment of almost \$24/kw relative to capital cost for lime dual alkali. (For a 1% S coal, all other factors being similar, operating cost savings would offset an additional capital cost of only about \$7/kw.) As a result, considerable effort was directed at development of a viable limestone dual alkali process in this program, even if the use of limestone increased the process complexity.

The various dual alkali modes are discussed in more detail in appropriate chapters of this report. A glossary for the dual alkali terminology is presented in each volume of this report.

III. LABORATORY AND PILOT PLANT SYSTEMS

A. LABORATORY METHODS

The effects of experimental variables on the kinetics and equilibria of several different reactions related to dual alkali regeneration have been studied during the course of the laboratory experimental program. For each of the several basic reactions studied, the general approach was first to conduct a series of batch experiments in which samples of the reacting mixture were taken periodically and analyzed to determine reaction rates and final equilibrium compositions. Additional studies were then carried out in a continuously fed stirred tank reactor (CSTR) to investigate the reaction further under conditions more representative of those in a continuous process situation.

Although a variety of reactions was studied, the experimental procedures were generally quite similar, since in most cases a solid reagent was reacted with a solution to produce a two-phase product slurry. The general experimental procedures used are presented in this section. In a few instances where a specific procedure was employed for a certain experiment, the procedural details are discussed along with the experimental findings. Determination of the chemical, physical and engineering properties of dual alkali product solids which are presented in Chapter VIII required that a number of special-purpose tests be performed; the details of those tests are presented in that chapter.

1. Experimental Apparatus, Operation and Sampling Procedures

Batch experiments were carried out in a 1-liter, three-necked, round-bottom flask, immersed in a controlled-temperature water bath. A magnetically driven stirrer provided mixing. To prevent oxidation during the course of the reaction, a slow constant purge of nitrogen was maintained over the reactor headspace.

Batch experiments were initiated by weighing appropriate amounts of the water soluble reactants (reagent grade materials were used exclusively) into the flask, adding the required amount of water, initiating the nitrogen purge, and stirring to effect dissolution. When dissolution was complete, a sample of the solution was first pipetted from the flask for analysis to establish the solution composition accurately, and then the solid reactant was added to the solution to initiate the reaction. Periodically, the reactor was opened momentarily to remove a sample of the reaction slurry for analysis; procedures used for phase separation and analysis are described below.

The CSTR system used was a rather simple apparatus shown schematically in Figure III-1. The reactor was a 1.5-liter glass vessel, commonly known as a resin kettle, fitted with an overflow sidearm positioned to yield a reactor volume of about 1 liter. Mixing was performed with an electrically

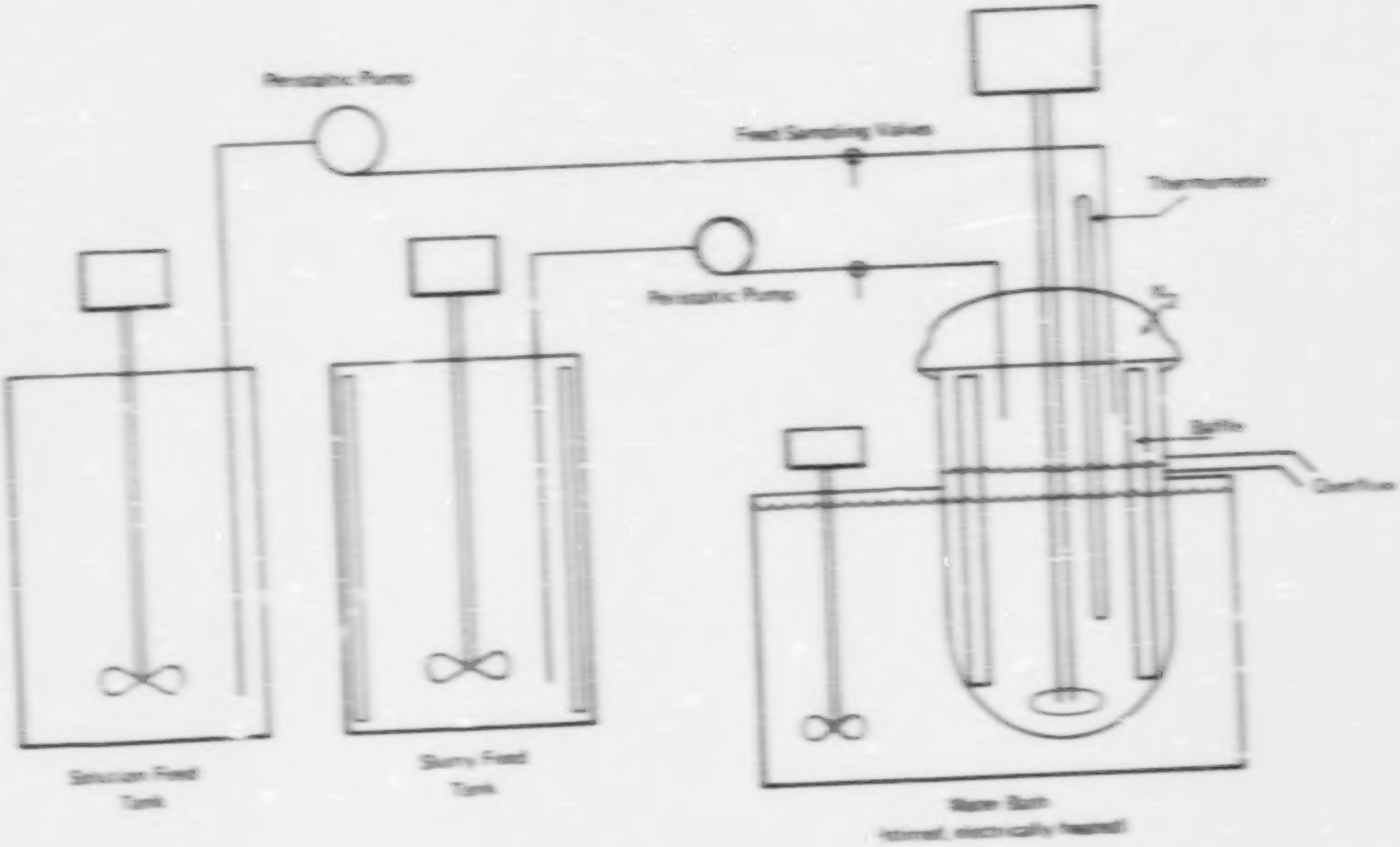

Peristaltic Pump
Feed Sampling Valves
Thermometer
N2
Peristaltic Pump
Baffle
Overflow
Solution Feed
Tank
Slurry Feed
Tank
Water Bath
(stirred, electrically heated)

FIGURE III-1 CONTINUOUSLY FED, STIRRED TANK REACTOR SYSTEM

driven stirrer, operating at about 700 rpm. Four rectangular pieces of Plexiglas (T.M. of Rohm & Haas Co.) about 2.0 cm wide and 0.3 cm thick, installed vertically around the sides of the reactor, served as baffles to ensure good vertical mixing. The lower portion of the reactor was immersed in a constant temperature bath for temperature control.

Reactant feed lines, a thermometer, an inlet for the nitrogen purge, and the stirrer shaft all entered the reactor through air-tight, ground glass joints in the lid; the lid and reactor bottom had mating ground glass surfaces which could be assembled air tight. During operation, the reactor headspace was purged with a flow of nitrogen which exited via the overflow sidearm.

Reactants were prepared and fed from two, stirred, 14-liter glass vessels with hermetically sealed stainless steel tops. The solid reagent was slurried with water, and fed from one tank (baffled) and the sodium sulfite/bisulfite/sulfate solution from the second. Reactants were pumped at controlled rates by variable speed peristaltic pumps (Sigma motor T68 and Masterflex 7565).

A list of all laboratory experiments is presented in Appendix A.

2. Analytical Procedures

The feed and effluent samples were collected and analyzed by procedures which permitted mass flow rates into and out of the reactor to be determined for each of the various chemical species of interest. Samples of solutions and slurries were collected for known periods of time in tared flasks and the total mass collected was determined gravimetrically. The slurries were then filtered, and the solids were washed thoroughly with a saturated calcium sulfate solution. The weight of the resulting wet cake was determined and a representative portion was taken and dried at 85°C. From the weights determined above, the measured weight loss upon drying, and the solution density, the mass flow rates of both phases of the slurry could be calculated.

Aliquots of liquids and dried solids were characterized by a variety of analytical techniques, most of them simple gravimetric or titrimetric procedures. The analytical methods employed were:

Parameter	Method
Sulfur (IV), TOS	Iodimetric Titration
Total Sulfur (Solids)	Oxidize, Weigh as $BaSO_4$
Total Sulfur (Solutions)	Titrate with Lead Perchlorate
Acidity/Hydroxide	NaOH/HCl Titration
Soluble Carbonate	Titration of $HCO_3^=$ with HCl

Solid Carbonate	Acidify, Collect CO_2 in NaOH, Titrate resulting solution as above
Calcium, Magnesium	EDTA Titration
Sodium, trace Mg^{++} and Ca^{++}	Atomic Absorption Spectrometry

Determination of the amount of Na_2SO_4 which reacted with lime or limestone to precipitate calcium sulfate from sodium sulfite/bisulfite/sulfate solutions was important in many of the laboratory experiments conducted. This determination required that the filtered product solids be washed thoroughly to remove entrained mother liquor without dissolving calcium sulfate from the solids. It was for this reason that a wash solution saturated with respect to $CaSO_4 \cdot 2H_2O$ was used for washing the solids. Prior to using this washing procedure routinely, analyses of dissolved calcium in the fresh and used wash solutions were performed to ascertain that no additional calcium sulfate was being introduced into the solids by the washing procedure.

The washed solids were subsequently analyzed for total sulfur, TOS, calcium, and sodium to permit the calculation of the amount of $CaSO_4$ present. Even after thorough washing (1 gram of dry solids washed with four, 25-ml portions of wash solution), a small amount of sodium, usually on the order of 3 mol percent of the total sulfur present, remained in the solids. That sodium was attributed to Na_2SO_4 entrapped within the calcium sulfite crystals, and it was excluded when calculating percent calcium sulfate in the solids. The percent calcium sulfate in the solids was calculated from the number of millimols of $CaSO_x$ and $CaSO_3$ per gram of total solids according to the relation

$$\text{Sulfate Precipitation} = \frac{CaSO_x - CaSO_3}{CaSO_x}$$

when $CaSO_x$ signifies the total of $CaSO_4$ and $CaSO_3$ in the precipitate.

Because this calculation involves taking a relatively small difference between two larger numbers, the result is quite sensitive to small analytical errors in the determination of $CaSO_x$ and $CaSO_3$. For example, in one actual case where calcium sulfate comprised 9.4% of the total calcium/sulfur salts, a 1% increase in the amount of $CaSO_x$ accompanied by a 1% decrease in the amount of $CaSO_3$ would have changed the calculated percent calcium sulfate content to 11.2%. Analytical uncertainty of that order is not unreasonable and its effect must be kept in mind when interpreting the experimental findings relating to sulfate precipitation.

B. PILOT PLANT

1. Description of the Facility

The dual alkali pilot plant at Arthur D. Little, Inc., (ADL) in Cambridge, Massachusetts, was built jointly by Combustion Equipment Associates (CEA) and ADL in 1973. The system operates on 2,000 acfm (400°F) of the combustion flue gas from a natural-gas-fired hot air furnace. SO_2 is added to the gas to provide any desired SO_2 concentration up to about 4,000 ppm.

The basic facility incorporates three process sections: gas scrubbing; absorbent regeneration; and solids separation. In addition, there are auxiliary process systems and equipment for special slipstream treatment operations. A schematic flow sheet of the major process units is provided in Figure III-2.

The scrubbing system includes a variable throat venturi scrubber followed by an absorption tower fitted with a radial vane demister. The absorption tower is equipped with removable trays and sprays so that it can be operated alternatively as a spray tower, a tray tower (with from one to three trays), or a de-entrainment separator.

The pilot plant has more than a dozen open-top tanks ranging in size from 8 gallons to 700 gallons for use as feed, storage, or hold tanks and reactor vessels. Two lime/limestone feed systems are available -- one for metering reactant as a dry solid and one for feeding reactant in slurry form.

The solids dewatering and separation system includes a 6-foot diameter Dorr-Oliver thickener with three overflow levels, and a Dorr-Oliver rotary drum vacuum filter. The filter has an active cloth area of 4.3 square feet and is equipped with a system of wash sprays which can be operated in a variety of spray configurations.

In addition to this basic process equipment, the pilot plant has a number of auxiliary units including: two Pfaudler kettles (one glass lined and one stainless); and a 6-inch Bird solid bowl centrifuge.

A list of all pilot plant operations is given in Appendix B.

2. Scrubber Operating Characteristics

The standard scrubber system for the EPA test program consisted of the venturi scrubber followed by the absorption tower with either two or three sieve trays. The configuration and operation of the tray tower depended upon the dual alkali mode being tested. In the concentrated active sodium modes, two trays were used with no recycle of absorbent liquor around the tray tower. Regenerated liquor was fed to the top tray on a once-through basis, the flow leaving the bottom tray being sent directly to the venturi recycle tank. In the dilute active sodium modes, three trays were normally used and liquor was recycled around the

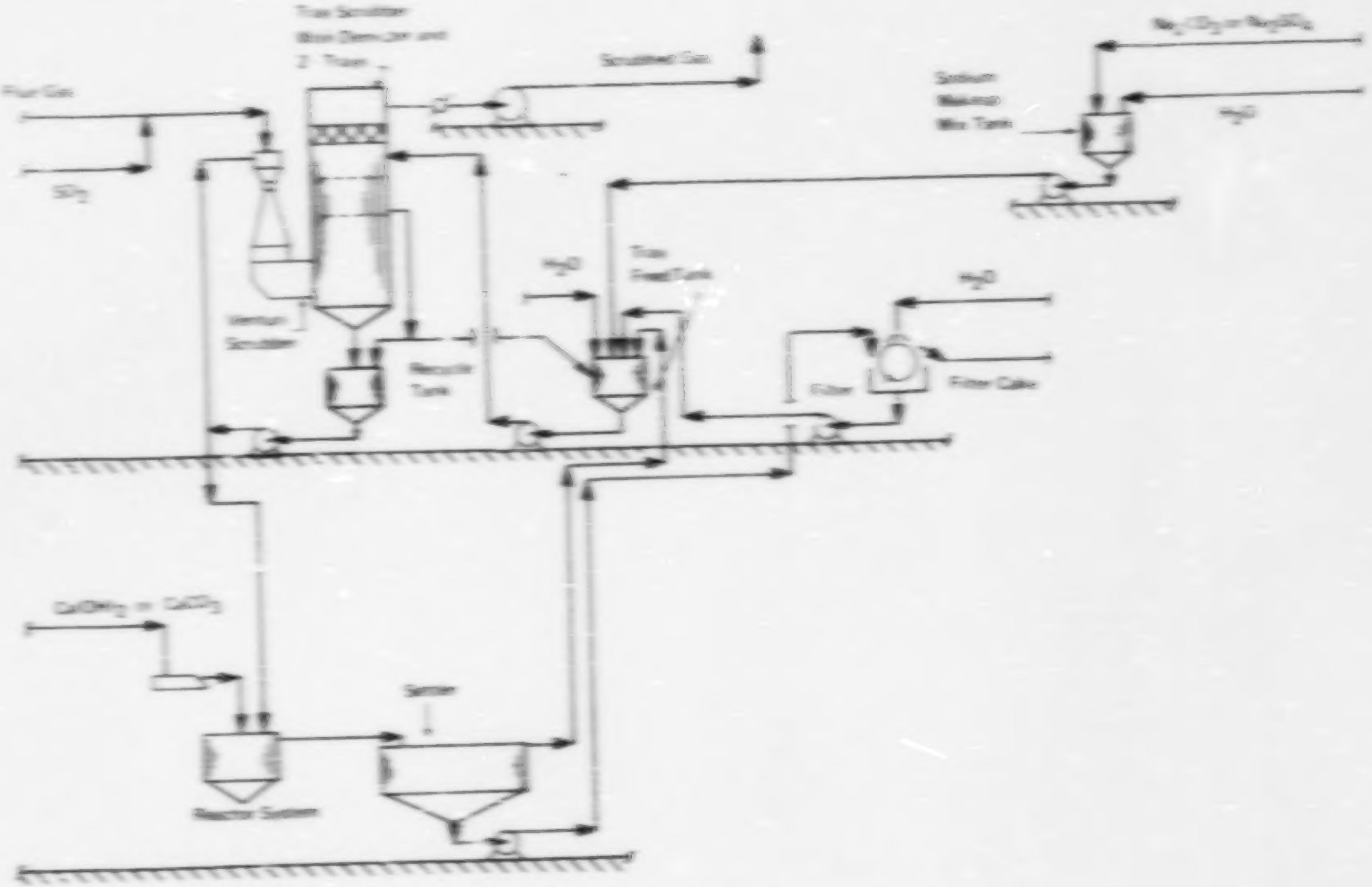

Tray Scrubber
With Demister and
2 Trays
Scrubbed Gas
Flue Gas
SO_2
Venturi
Scrubber
Recycle
Tank
H_2O
Tray
Feed Tank
H_2O
Filter
Filter Cake
Sodium
Makeup
Mix Tank
Na_2CO_3 or Na_2SO_3
H_2O
$Ca(OH)_2$ or $CaCO_3$
Settler
Reactor System

FIGURE III-2 SCHEMATIC FLOW DIAGRAM OF DUAL ALKALI PILOT PLANT

tray tower to control pH and minimize CO_2 absorption. Scrubber system details are given in the flow sheets for each mode in the appropriate sections of the report.

The range of operating conditions of the scrubber system is given in Table III-1. There was no washing of the radial vane demister either with water or scrubber liquor in any of the modes; and, since there was no fly ash in the inlet flue gas, the spray beneath the bottom tray was not used.

It is important to realize that the primary function of the scrubber throughout most of the pilot plant testing was to provide scrubber bleed liquors of compositions within the range desired for the tests being performed. However, the scrubber system was also used to assess calcium scale potential (particularly in dilute mode runs) in certain operational modes to evaluate the ease of operation.

The general operational characteristics of the scrubber system with regard to SO_2 removal and absorbent oxidation are reviewed below. As appropriate, specific operating conditions and performance characteristics of the scrubber section are covered later in the discussions of operations in each mode.

a. SO_2 Removal

The SO_2 removal efficiency in the pilot plant scrubber system has been evaluated in a number of previous studies as well as during this program. The overall SO_2 removal has been shown to be a function of the system feed stoichiometry, the scrubber configuration, the inlet SO_2 level, and, to a lesser extent, the concentration of TOS in the absorbent liquor and the rate of sulfite oxidation.

The feed stoichiometry is given by:

$$\frac{\text{mols active Na}^+\text{ capacity}}{\text{mols SO}_2\text{ inlet}}$$

The active Na^+ capacity is the theoretical equivalent of the mols of SO_2 which can be absorbed by active sodium species:

$$[Na^+]_{active}\text{ capacity} = [Na_2SO_3] + 2[Na_2CO_3] + [NaOH] + [NaHCO_3]$$

The relationship between SO_2 removal and feed stoichiometry for the venturi/two-tray configuration operating in the concentrated active sodium mode is shown in Figure III-3. The data indicate that for a given stoichiometry, lower SO_2 levels tend to result in slightly lower removal efficiencies. The plot shows that to achieve a 90^+% removal of SO_2 from a gas containing 2,500 ppm, a feed stoichiometry of about 1.1

Table III-1 SCRUBBER SYSTEM OPERATING CONDITIONS

Flue Gas Conditions

Temperature Entering Venturi (Adjustable): 365 - 430°F
Inlet Flow Rate (Adjustable): 1,100 acfm
NO_x Level: 800 - 1,000 ppm
SO_2 Level (Adjustable): 500 - 2,800 ppm
O_2 Level (Adjustable): 4 - 10% (dry basis)
H_2O Level: 18 - 23% (dry basis)
Gas Dew Point: 120 - 130°F

Venturi Scrubber Conditions

Venturi Tank Temperature: 160 - 165°F
Venturi Recycle Flow: L/G = 16 gals/Macfm sat'd
Venturi Pressure Drop: 10 - 14 in. H_2O

Tray Tower Conditions (Two Sieve Trays)

Tray Tower Feed: L/G = 1.5 - 12 gals/Macfm sat'd
Pressure Drop/Tray: 1.6 - 2.0 in. H_2O

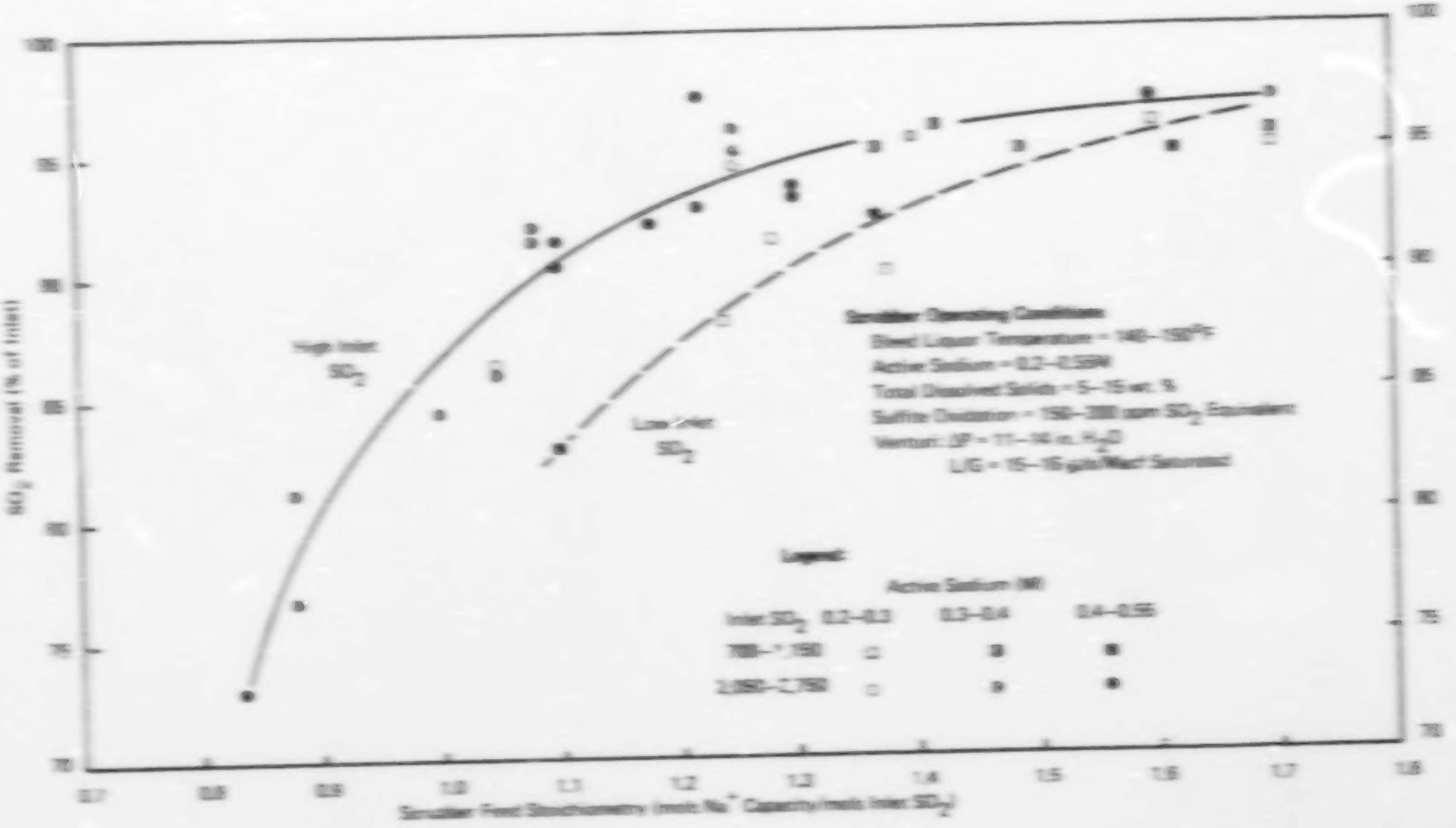


FIGURE 6–3 SO_2 REMOVAL VS. FEED STOICHIOMETRY (VENTURI + 2 TRAYS)

is required, while to achieve the same 90+% removal from a gas containing about 700 ppm, a feed stoichiometry of about 1.3 is required. This trend would be expected since at higher SO_2 levels there is a greater driving force for removal; hence, higher removal efficiencies are more easily attained.

This is somewhat different than the experience in a direct lime/limestone scrubbing system where SO_2 absorption is limited by liquid phase and solid/liquid mass transfer. In sodium absorption above feed stoichiometries of 1.1, gas phase mass transfer becomes the limiting rate.

Within the ranges examined, there was no effect observed of active sodium or total dissolved solids concentration on SO_2 absorption.

b. Scrubber Oxidation Rates

In general, oxidation of sulfite in the scrubber system is a function of the oxygen content of the flue gas, the scrubber configuration, the concentration of sulfite, and the total dissolved solids concentration. Under most conditions, oxidation has been found to be oxygen mass transfer limited. Thus, the rate of sulfite oxidation increases with increasing gas/liquid contacting (number or efficiency of contact stages) and increasing oxygen content of the flue gas, and decreases with increasing dissolved solids level (decreasing oxygen solubility). The concentration of the sulfite ion itself (independent of total dissolved solids) was only found to affect oxidation at low concentration levels. The rate of sulfite oxidation (mols sulfite oxidized/unit time) was found to be essentially independent of active sodium concentration between 0.20M and 0.65M active Na^+, all other variables being equal. However, oxidation decreased roughly proportionally to active sodium concentration at levels below about 0.20M active Na^+, indicating that oxidation was becoming reaction rate limited. Also, the presence of trace elements such as those from fly ash can promote or inhibit sulfite oxidation.

Figures III-4 and III-5 show oxidation data taken in the pilot plant using the venturi/two-tray configuration. Figure III-4 shows the effects of active sodium concentration at low total dissolved solids levels and 4-5% oxygen in the flue gas. Figure III-5 shows the effects of both oxygen content in the flue gas and total dissolved solids levels on oxidation. At intermediate active sodium concentrations (0.3-0.6M Na^+_{active}) and 1.5-2.5M total sodium, the oxidation rate (mols sulfite oxidized expressed in equivalent ppm of SO_2 absorbed) at 5% oxygen was 200-250 ppm of SO_2. This would correspond to about 8-10% of the SO_2 removed for 3.5% sulfur coal and 20-25% for 1.5% sulfur coal. At 2-3 times the total dissolved solids concentrations, rates of oxidation were reduced by about 50% or more.

The data presented in Figures III-4 and III-5 are a combination of data taken prior to and during the EPA test program. Each point in Figure III-5 represents the average of from three to six data points for a given run. In all cases the rate of oxidation across the scrubber was calculated from sodium, sulfite and sulfate balances across the system and confirmed by

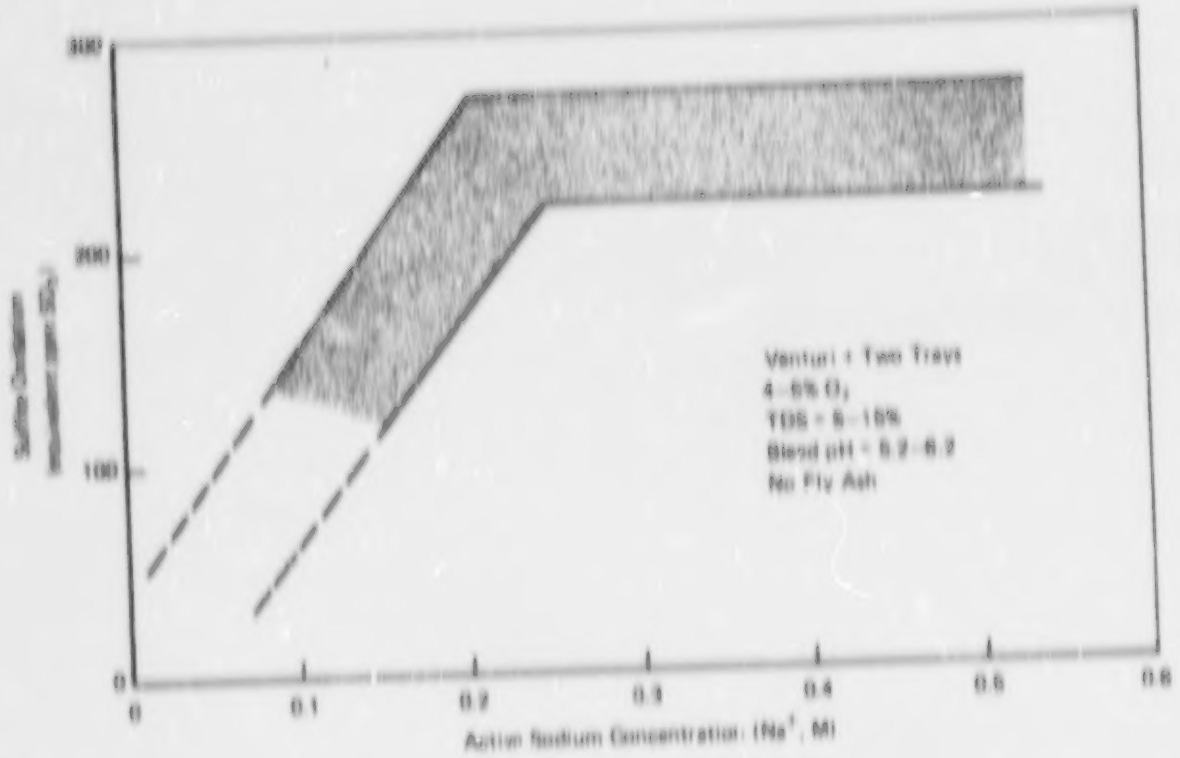


FIGURE III-4 SCRUBBER OXIDATION – EFFECT OF ACTIVE SODIUM CONCENTRATION

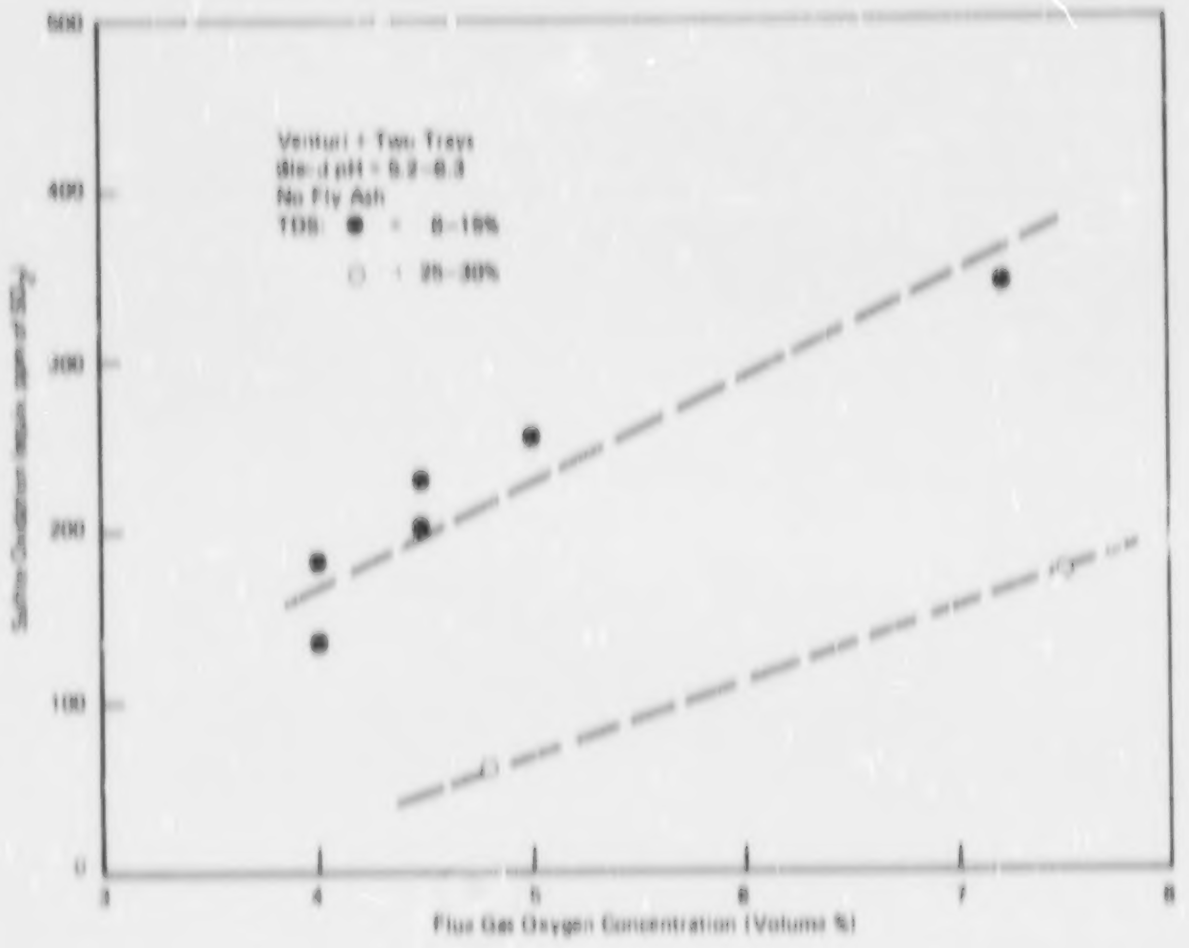


FIGURE III-5 SCRUBBER OXIDATION – EFFECTS OF OXYGEN AND TDS CONCENTRATION

overall material balances and cake analyses (taking into account oxidation occurring in other parts of the system).

It should be noted that these oxidation and SO_2 removal data were obtained at scrubber liquor operating temperatures which were 15-20°F higher than those which would be expected in a scrubber operating on a normal utility or industrial boiler. The higher temperatures were due to the fact that the flue gas was generated from natural gas fuel which has a much lower carbon-to-hydrogen ratio than coal, and which when burned produces combustion product gas with considerably higher humidity levels. These higher humidity levels result in higher saturated gas temperatures in the scrubber which affect both SO_2 removal and sulfite oxidation rates. The equilibrium vapor pressure of SO_2 is on the order of 50-60% higher, so it would be expected that the removal efficiencies observed in the pilot plant would be lower than those attainable in actual boiler applications. Similarly, the rate of sulfite oxidation is strongly dependent upon temperature, increasing with increasing temperature. Thus, the oxidation rates observed in the pilot plant may also be slightly high compared to those expected in actual applications.

This is confirmed by data obtained in the prototype system at the Scholz Steam Plant where oxidation rates at 4.5-5.0% oxygen in the flue gas were found to be 150-200 ppm compared with the 200-250 ppm for the pilot plant (using the same venturi/two-tray combination). Similarly, oxidation rates at 7.5% oxygen averaged about 250 ppm in the Scholz system and between 300 ppm and 350 ppm in the pilot plant.

c. Conclusions

The pilot plant SO_2 removal and oxidation data are specific to the pilot plant scrubber configuration as influenced by the scrubber operating temperature for the pilot plant flue gas stream. The scrubber operating temperature of 140-150°F is higher than that normally encountered in conventional boiler flue gas applications (120-130°F). The elevated temperature in the pilot plant system tends to decrease SO_2 removal efficiency due to elevated SO_2 partial pressures for any given solution, and tends to increase oxidation rates. However, the purpose of the pilot plant scrubber and its operations was to provide scrubber effluent with an appropriate composition for use in the various dual alkali modes rather than to generate basic data on SO_2 absorption using sodium solutions.

Within the above constraints, the scrubber operations did indicate that SO_2 removal in excess of 90% is easily accomplished over a range of SO_2 inlet concentrations from 700-2,800 ppm by adjusting the scrubber feed stoichiometry. To achieve this removal efficiency, a stoichiometry of 1.1 mols of active Na^+ capacity/mol SO_2 inlet was required at the high inlet SO_2 range; a stoichiometry of 1.3 was required in the lower inlet SO_2 range. In any range of SO_2 concentration, increasing stoichiometry increased the SO_2 removal. There was no important apparent effect of active sodium concentration within a range of 0.2-0.5M or total dissolved solids concentration within a range of 5-15 wt %.

Sulfite oxidation is mass transfer limited at active sodium concentrations above 0.2M with the rate of oxidation increasing with the oxygen content of the flue gas. At lower active sodium concentrations the oxidation rate is roughly proportional to the active sodium concentration. The rate of oxidation decreases with increasing total dissolved solids; by increasing TDS from 8-15 wt % to 25-35 wt %, the oxidation rate being reduced by a factor of 2-3. At lower total dissolved solids in concentrated active sodium systems (0.3-0.6M active Na^+, 5-15 wt % TDS) sulfite oxidation can be expected to be on the order of 100-300 ppm equivalent SO_2 removal for oxygen concentrations in the flue gas ranging from 4 to 8 vol %.

IV. LIME REGENERATION -- CONCENTRATED ACTIVE SODIUM MODE

A. PRIOR WORK ON LIME REGENERATION AT ADL

Prior to initiation of the EPA/ADL Dual Alkali Program, laboratory and pilot plant research and development were conducted at ADL on lime regeneration of concentrated scrubbing solutions. In 1971 ADL conducted a detailed laboratory study of the regeneration of simulated sodium scrubbing solutions using hydrated lime. This work, sponsored by the Illinois Institute for Environmental Quality,[4] dealt exclusively with characterizing the nature of the regeneration reaction. The objectives of the laboratory program were the development of reaction conditions which would produce waste calcium salts with good settling and filtration characteristics, production of scrubber feed solutions with low concentrations of dissolved and suspended calcium salts, and good utilization of lime in the regeneration reaction.

The objectives of these laboratory studies were satisfied and conditions for an effective regeneration reaction were determined. Chemical analyses in the laboratory at that time were limited to liquid phase analyses; because of the generally high sulfate concentrations in the reactor feed, changes in sulfate concentration were usually within the experimental error of the analyses. As a consequence, no significant sulfate precipitation was detected in the lime regeneration of concentrated sulfite solutions.

The dual alkali process still appeared attractive because of the highly effective SO_2 removal, very low calcium concentrations in the regenerated scrubber feed, and the effectively complete utilization of lime in the process. Based upon the laboratory results, the dual alkali pilot plant was constructed at ADL's facilities. The pilot plant was operated to generate the design data for the 20-megawatt prototype dual alkali system to be built by CEA for Gulf Power Company/Southern Company Services.

As part of those pilot operations, analytical techniques were developed for the solids generated in the dual alkali system. Analyses indicated that pilot plant solids contained 10-20% of the calcium sulfur salts as calcium sulfate and that simultaneous calcium sulfate precipitation was occurring, to a limited extent, with precipitation of calcium sulfite in concentrated scrubbing solutions. Care was exercised in analysis to ensure that the sulfate found in the solids was neither occluded Na_2SO_4 nor precipitated calcium sulfite which had later oxidized to calcium sulfate.

The results of the laboratory and pilot work conducted prior to the EPA/ADL program are summarized in the literature.[5]

B. LABORATORY STUDIES OF SULFATE PRECIPITATION WITH LIME

1. Introduction

The observation during ADL pilot plant tests that calcium sulfate was present in the product solids when regenerating with lime in a concentrated active sodium mode aroused a great deal of interest because in a concentrated mode the removal of sulfate produced as a result of sulfite oxidation was foreseen as a possibly significant problem. From a consideration of the thermodynamic equilibria involved, one would not expect calcium sulfate to precipitate during regeneration of concentrated sodium sulfite/bisulfite/sulfate solutions.

In a typical regenerated solution produced by a concentrated mode process, the pH would be in the range 9-11, and would contain about 0.50M Na_2SO_4 and 0.25M Na_2SO_3. Equilibrium levels of total dissolved calcium would be typically less than 100 ppm (0.0025M). In a solution of this ionic strength (about 2.3M), for calcium sulfate to precipitate as gypsum ($CaSO_4 \cdot 2H_2O$), the apparent solubility product, K_{sp}' (the product of total dissolved calcium and total sulfate concentrations), is about 1.05×10^{-2}. For the 0.50M Na_2SO_4 level taken as an example, a dissolved calcium level of 0.021M (about ten times greater than the actual level) would be required to effect the precipitation of gypsum.

Subsequent to observing the presence of calcium sulfate in the solids produced at the ADL dual alkali pilot plant, Borgwardt[5] demonstrated quite conclusively during pilot studies of direct limestone slurry scrubbing that calcium sulfite product solids containing significant amounts of calcium sulfate from liquors that were unsaturated with respect to gypsum could be produced. A distinct gypsum or anhydrite (anhydrous $CaSO_4$) crystalline phase in the solids could not be identified and it was proposed that the calcium sulfate was present as some sort of solid solution within the $CaSO_3 \cdot 1/2H_2O$ crystal. Further, it was found that the ratio of $CaSO_4/CaSO_3$ in the solids could be correlated quite well with the activities of the sulfate ion in the liquor.

The laboratory program which was conducted to study this apparently similar phenomenon in the concentrated lime dual alkali process consisted of a series of continuously fed, stirred tank reactor (CSTR) experiments. They were designed first to verify under "normal" operating conditions that sulfate was, in fact, being precipitated and then to study the effects of Na_2SO_4 and active sodium levels on the amount of sulfate precipitation. Studies were also conducted to determine the effect on sulfate precipitation of less than complete neutralization of bisulfite, regeneration with shorter and longer than normal reaction times, and higher and lower than normal levels of active sodium.

The normal reactor residence time for these experiments was established at 30 minutes, a time, based on previous ADL experience, that was adequate for completion of reactions, even if regeneration was carried well into the hydroxide range. The solution fed to the reactor normally contained about 0.5M active sodium and had a pH in the range from 5.4 to 5.6 ($HSO_3^-/SO_3^=$ ratio approximately 10). As noted earlier in the description of the laboratory apparatus, lime was fed to the reactor as a 5-10% slurry which diluted the sodium fed by 10-20% upon mixing in the reactor. In the subsequent discussions, when reactant concentrations are reported, they are after dilution by the slurry water.

3. Experimental Results

The precipitation of calcium sulfate observed under normal conditions at several levels of dissolved sulfate is tabulated, along with the associated solution compositions, in Table IV-1. The first two experiments, PN13 and 10 are essentially identical except for the change in concentration of Na_2SO_4 from about 0.20M to about 0.55M. In both cases measurable amounts of sulfate precipitation were observed -- precipitation increased with increasing sulfate concentration. In experiment PN10, regeneration was carried out to the point where the HSO_3^- fed to the reactor was just 100% neutralized and no free hydroxide was generated (sulfate precipitation was 0.091 mole $CaSO_4$ per mol $CaSO_x$).

Since in certain cases it proved difficult to adjust reagent flows to achieve exactly 100% neutralization of the HSO_3^- present, and in other experiments, the degree of regeneration was intentionally varied, the term "percent neutralization" was used to define the extent to which regeneration was carried out. When the bisulfite present was not completely neutralized, the percent neutralization was computed from the relation

$$\text{Percent Neutralization} = \left[\frac{[HSO_3^-]_{\text{initial}} - [HSO_3^-]_{\text{final}}}{[HSO_3^-]_{\text{initial}}}\right] \times 100\%$$

When regeneration was carried on into the free hydroxide region, the neutralization was greater than 100% and was calculated from the relation

$$\text{Percent Neutralization} = \left[\frac{[HSO_3^-]_{\text{initial}} + [OH^-]_{\text{final}}}{[HSO_3^-]_{\text{initial}}}\right] \times 100\%$$

Experiment PN9 was similar to experiment PN10 except that percent neutralization was increased from 100% to 124% to determine the effect of the extent of regeneration on sulfate precipitation. However, the sulfate precipitation (0.090) was essentially identical to that observed at 100% neutralization. In experiment PN14, the concentration of sulfate was further increased to about 1.1M, and sulfate precipitation increased to 0.165 of the total precipitate. Experiment PN14 was carried to only 67% neutralization; however, results of subsequent studies established that Na_2SO_4 level, rather than incomplete neutralization, was the more significant factor in the increased amount of calcium sulfate precipitation observed.

[illegible]

[illegible]

[illegible]	[illegible]				[illegible]						[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	pH	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	pH			
[illegible]	[illegible]	[illegible]	[illegible]	5.3	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	7.0	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	5.4	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	8.3	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	5.4	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	11.5	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	5.4	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	6.8	[illegible]		[illegible]

---

[a] [illegible]

[b] [illegible]

The sulfate precipitated in these experiments is shown as a function of sulfate concentration in Figure IV-1. Within experimental error, sulfate precipitation was directly proportional to sulfate concentration in the reactor. (It should be remembered from the discussion of experimental error in Chapter III that sulfate precipitation is subject to some experimental error -- for a true precipitation of 0.08, experimental error could cause the measured value to be in the range from 0.06-0.10.) Included in Figure IV-1 are the results of additional experiments carried out at much shorter residence times (5 minutes and 8 minutes) at 100% neutralization, but at the same active sodium level as experiments PN13, PN10, PN9 and PN14. With the possible exception of the experiment at 0.2M Na_2SO_4 and 5 minute residence time, calcium sulfate precipitation and its dependence on sodium sulfate concentration were essentially the same as that observed at the normal, 30 minute residence time. Also included in Figure IV-1 is the effect of allowing portions of reactor effluent slurry to stand with gentle stirring for a period of three hours after emerging from the reactor. In every case, a decrease in the mol ratio $CaSO_4/CaSO_3$ in the solids was observed upon standing.

The effect of percent neutralization was studied in detail with the CSTR operating at a 5 minute residence time followed by a three-hour hold time to observe the effect of hold time on reaction products, equilibria, and product stability. Observed sulfate precipitation is shown in Figure IV-2 as a function of percent bisulfite neutralized. In these studies, active sodium (after dilution) and the pH of the feed were maintained at "normal" levels, except for the several cases where specifically indicated, the concentration of Na_2SO_4 was between 0.64M and 0.69M. In those cases where the Na_2SO_4 concentration fell outside that range, the arrows indicate approximate adjustments to sulfate precipitation which would have been expected at a sodium sulfate concentration of 0.67M (based on the Na_2SO_4 dependence shown in Figure IV-1). Although there is some scatter in the data, increased sulfate precipitation seemed to occur at very high and very low percent neutralizations. Also shown in Figure IV-2 is the general decrease in $CaSO_4/CaSO_3$ in the solids when the product slurry was allowed to stand and react for an additional period of three hours.

Sulfate precipitation as a function of the concentration of TOS was studied at an 8 minute CSTR residence time and the results observed are shown in Figure IV-3. Except where specifically indicated, a CSTR residence time of 8 minutes was employed and the concentration of Na_2SO_4 was about 0.6M. Two of the data points were obtained from experiments in which a 5 minute CSTR was used. The experiment at 0.65M TOS had a higher sulfate concentration, 0.75M Na_2SO_4. Based on the relationship of calcium sulfate precipitation to Na_2SO_4 concentration discussed previously, the arrows attached to the data points for that experiment indicate what the $CaSO_4/CaSO_3$ mol ratio should have been at 0.6M Na_2SO_4.

The data in Figure IV-3 show a clear inverse proportionality between the amount of calcium sulfate precipitated and the TOS concentration. Because of the relatively small number of data points obtained and the scatter in them, a precise determination of the functional relationship between TOS

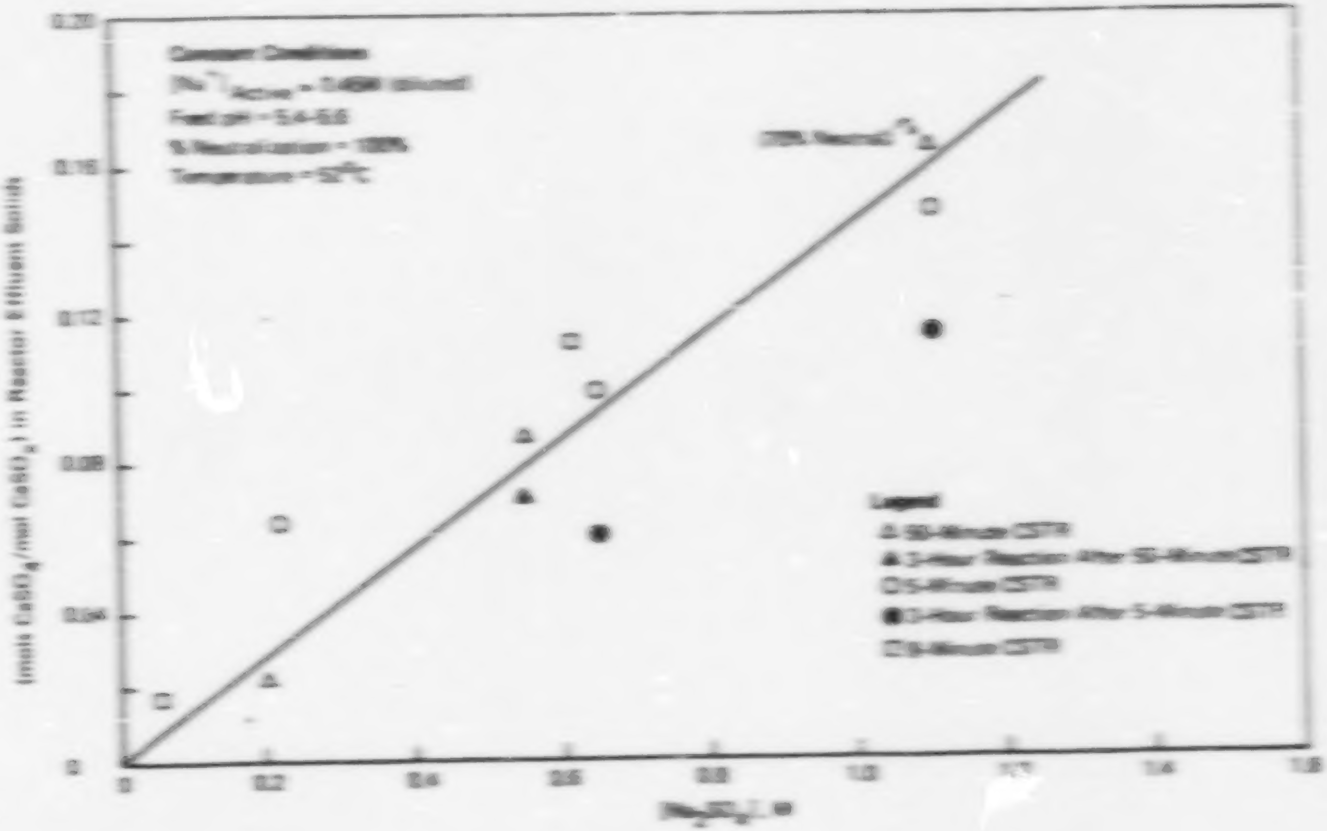


FIGURE IV-1 SULFATE PRECIPITATION AT VARIOUS Na_2SO_4 CONCENTRATIONS

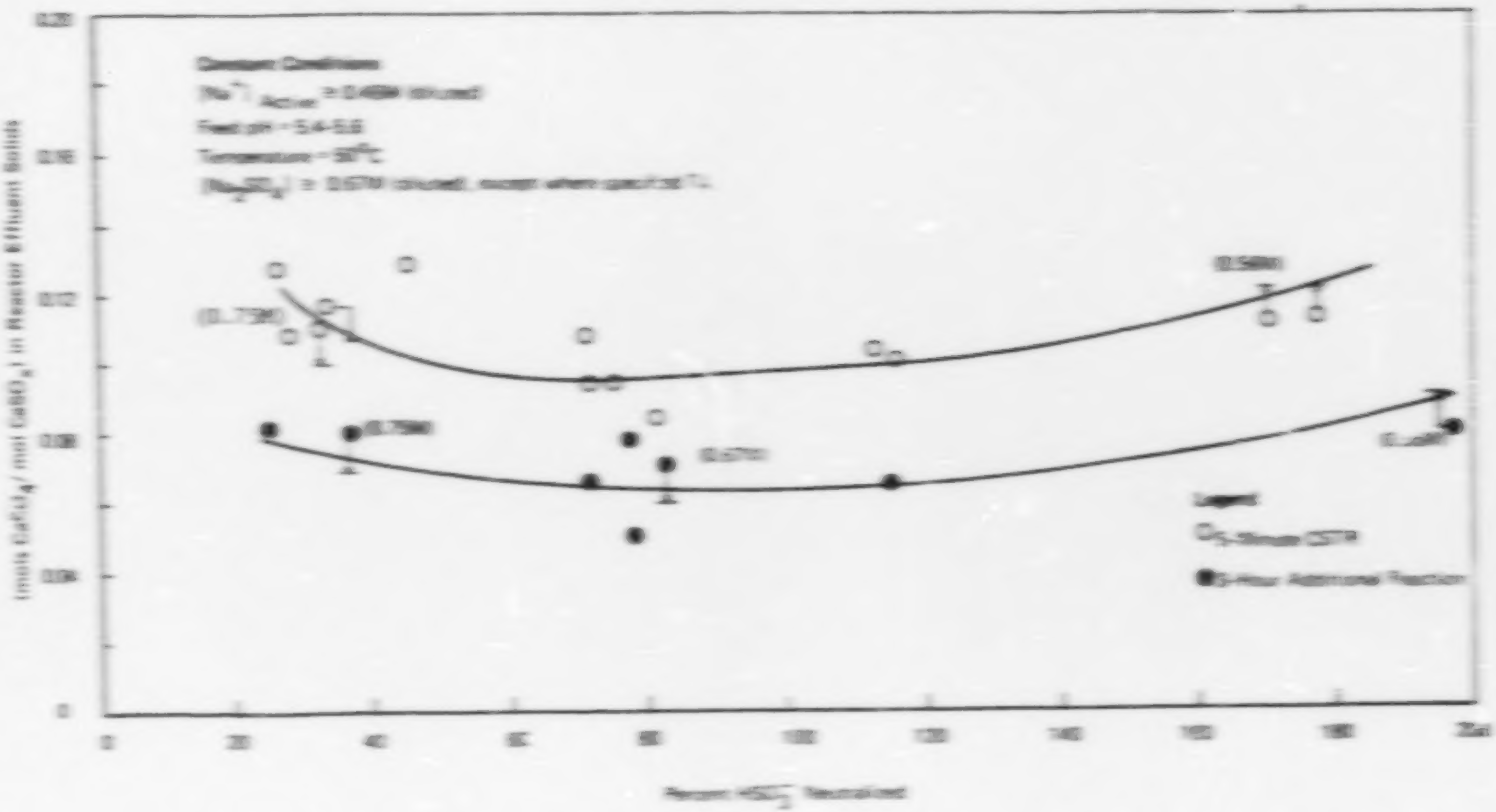


FIGURE IV-2 SULFATE PRECIPITATION FOR VARIOUS DEGREES OF LIQUOR REGENERATION

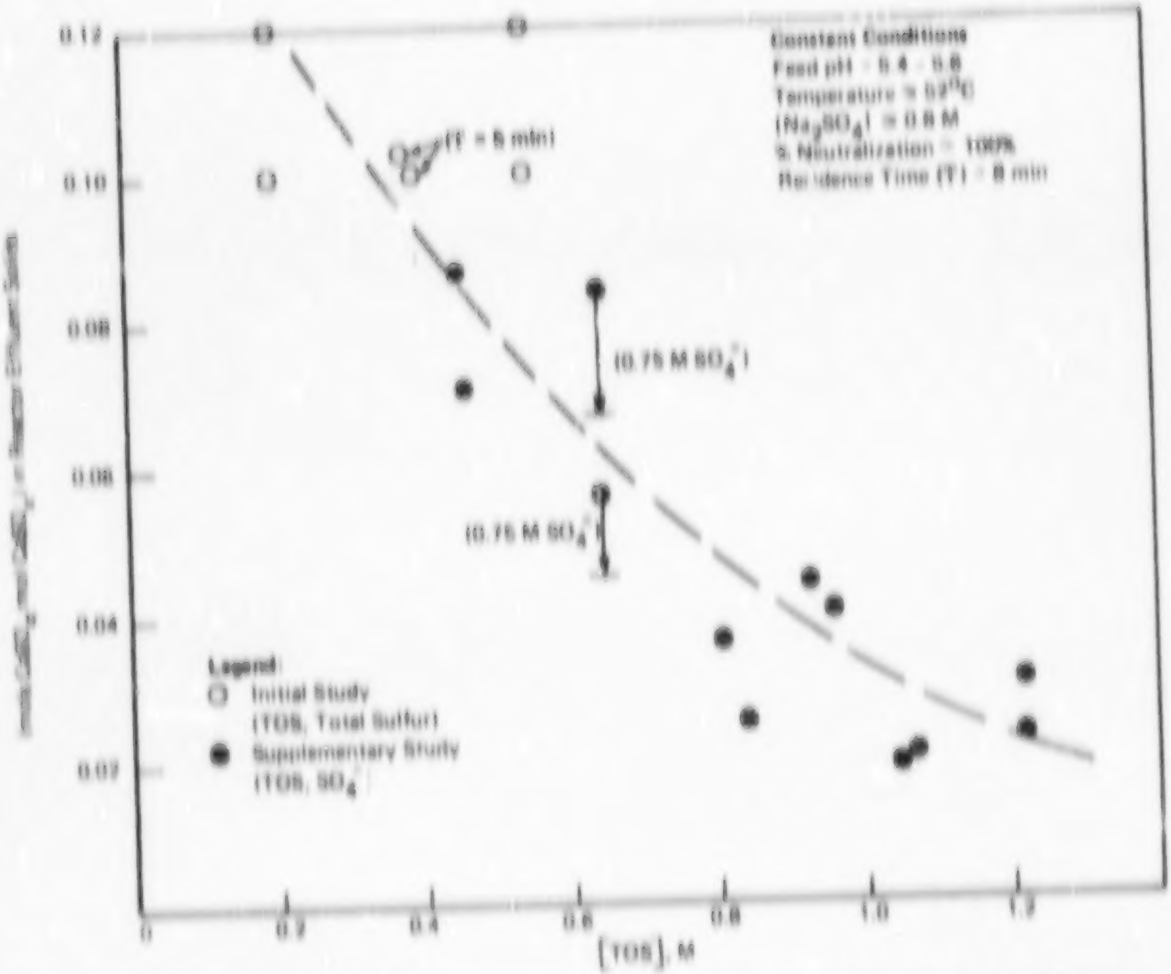


FIGURE IV-3 EFFECT OF TOS CONCENTRATION ON CALCIUM SULFATE PRECIPITATION REGENERATION WITH LIME

concentration and calcium sulfate precipitation based only on laboratory data was not attempted. A general correlation of all laboratory and pilot plant data is presented in Section C of this chapter.

3. Discussion

The experimental work described was aimed primarily at developing a practical understanding of what variables are important to, and in what manner they influence, calcium sulfate precipitation. The experimental results clearly establish that calcium sulfate can be precipitated when concentrated sodium sulfite/bisulfite/sulfate solutions are reacted with lime.

The direct proportionality between one of the two most significant independent variables, Na_2SO_4 concentration, and the percent $CaSO_4$ in the product solids is not surprising since, simplistically, increasing the $SO_4^=/SO_3^=$ ratio should favor precipitation (or inclusion) of $CaSO_4$ into the calcium sulfite. The observation that sulfate precipitation decreased when the concentration of TOS was increased is also reasonable. At constant pH, $SO_3^=$ concentration is directly proportional to the concentration of TOS. Finally, the somewhat lower $CaSO_4/CaSO_x$ ratio observed at intermediate percent neutralizations is also reasonable because $SO_3^=$ concentration is relatively higher in that region than at either extreme.

A general decrease in $CaSO_4/CaSO_x$ mol ratio when the effluent slurry from the 5 minute CSTR was allowed to continue to react obviously indicates that the solids in the initial effluent were not at equilibrium with the solution. The initial effluent liquid phase tended to be supersaturated with respect to $CaSO_3$ as evidenced by the subsequent appearance of solids (largely $CaSO_3 \cdot 1/2H_2O$) when samples of filtered reactor effluent were allowed to stand. However, the changes in total dissolved calcium which occurred when the intact slurry samples were allowed to stand could have produced only about 10% of the change in $CaSO_4/CaSO_x$ observed even if desupersaturation had resulted in the precipitation of only calcium sulfite. In some of the slurry samples, lime continued to react with the solution after the first 5 minutes of reaction, resulting in the precipitation of additional calcium sulfite, but that, in itself, could have changed the $CaSO_4/CaSO_x$ ratio by only 10-20% of the amount observed. Thus, it was concluded that although the amount was small and difficult to measure accurately, some of the $CaSO_4$ which initially had precipitated had, in fact, redissolved as the mixture was allowed to equilibrate.

In no case were the measured levels of total dissolved calcium and sulfate high enough to even approach saturation with respect to gypsum. Values of K_{sp}', the "apparent solubility product", which were observed under a number of reaction conditions are shown in Figure IV-4. The solid curve represents the calculated value of K_{sp}' as a function of ionic strength for solutions saturated with respect to gypsum. These values of K_{sp}' were calculated by the method of Kusik and Meissner,[7] which was developed to deal with solutions at high ionic strengths.

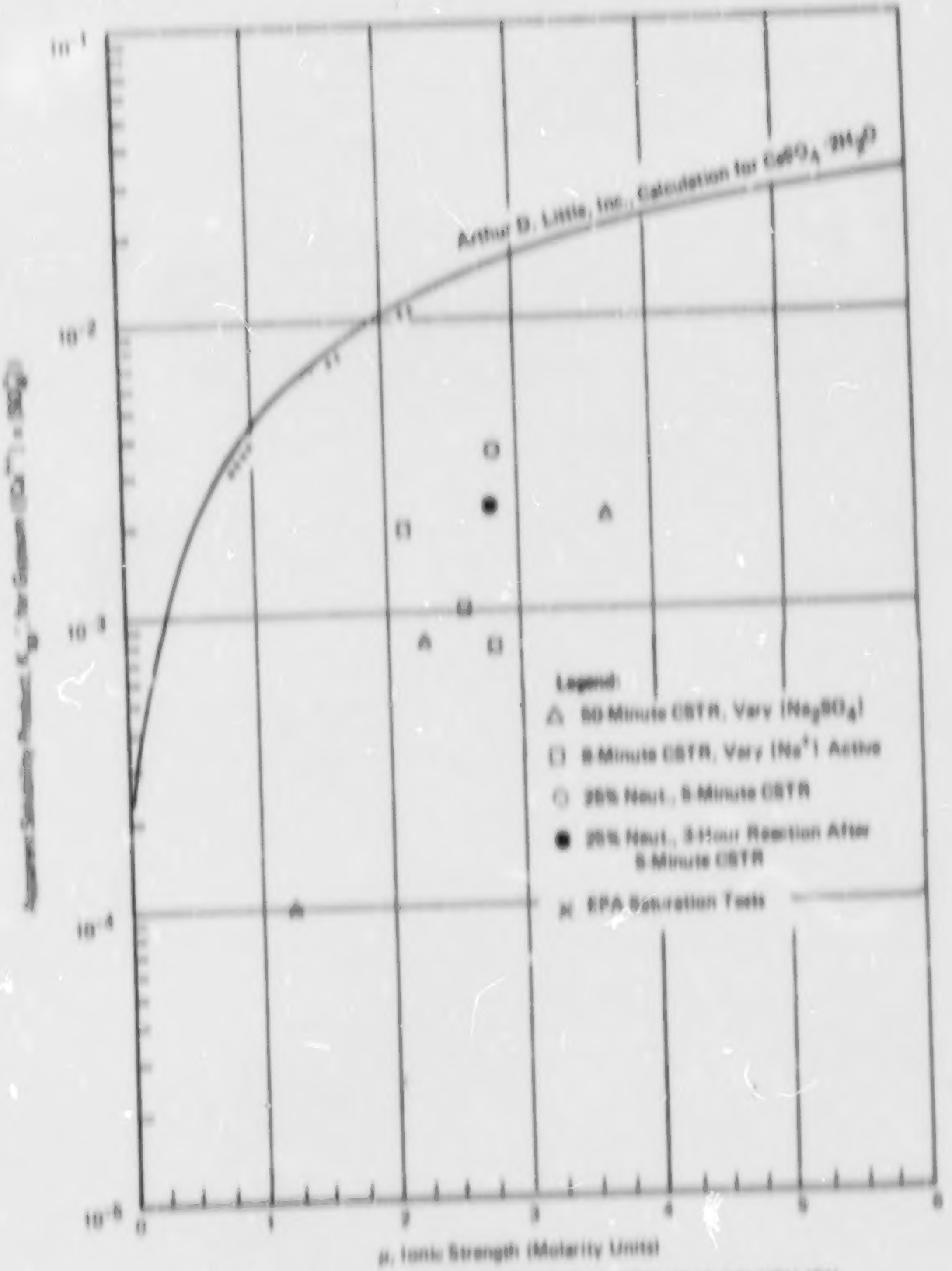


FIGURE IV-4 RELATION OF OBSERVED APPARENT SOLUBILITY PRODUCTS TO SATURATION VALUES FOR GYPSUM

This method involves first estimating the reduced activity coefficient of "pure" $CaSO_4$ (or $CaSO_3$) at total ionic strength, μ, of the multicomponent solution; such a solution normally would be supersaturated. Then the activity coefficient, γ, of $CaSO_4$ (or $CaSO_3$) in the multicomponent solution is obtained which is normally different from the pure solution value calculated above. After determining the water activity, a_w, the resulting values are substituted into the appropriate thermodynamic solubility product $[(K_t)_{sp}]$ expression

$$(K_t)_{sp} = m_{Ca} m_{SO_4} \gamma^2 a_w^n$$

where n is the number of waters of crystal hydration and m is the molality of the calcium and sulfate (or sulfite) ion as indicated by the subscript.

The accuracy of the predicted values of K_{sp}' is confirmed by the close agreement between the calculated values as shown by the curve and experimental values derived from EPA experiments in which dual alkali reaction effluent slurries were saturated with gypsum (Chapter VIII) during saturation tests.

C. PILOT PLANT OPERATIONS -- CONCENTRATED ACTIVE SODIUM MODE

1. Pilot Plant Test Program

The evaluation of the dual alkali process operation in the concentrated active sodium mode using slaked lime for absorbent regeneration was focused primarily on the performance of the regeneration system at active sodium levels above 0.25M. The operation of the regeneration reactor system ultimately determines the required calcium/SO_2 stoichiometry as well as the properties of the waste solids produced, both of which are important factors in determining the operability and economics of this dual alkali approach.

The pilot plant test program involved the characterization of two different reactor systems: a continuous stirred tank reactor (CSTR); and a multistage reactor system previously developed by ADL (ADL reactor), which for this study consisted of two CSTR's in series. The holdup time in the first stage is usually maintained between five minutes and ten minutes and in the second and later stages between 20 minutes and 40 minutes each. While all reactants are normally fed to the first stage, the reactor has been tested with split feeds.

Standard operating conditions for the ADL reactor were established for the two-stage system in pilot plant development work prior to this EPA program; however, data on the operation of a CSTR in the concentrated active sodium mode were not complete. A preliminary study of the CSTR, therefore, was undertaken in the pilot plant to examine the effects of various reactor parameters and selected process variables on the performance of the CSTR, and to develop a set of suitable operating criteria. The preliminary study consisted of short-term, open-loop reactor runs using simulated scrubber bleed and dry hydrated lime. This initial phase of testing was then followed by a number of extended, closed-loop continuous runs to confirm the open-loop results and to evaluate the overall process operation using both the CSTR and a two-stage ADL reactor.

The lime used in all the pilot plant runs was a 200-mesh hydrated lime containing 95 wt % calcium (reported as $Ca(OH)_2$) and averaging 91 wt % available calcium hydroxide. The remaining 4 wt % calcium, consisting mainly of $CaCO_3$ and burnt CaO, was determined to be essentially unavailable for reaction above a pH of 8.

2. Regeneration Reactor Performance

Reactor performance in both the open-loop reactor tests and the closed-loop continuous runs was evaluated in terms of four process criteria: calcium utilization; effluent soluble calcium concentration; reaction of sodium sulfate to precipitate calcium sulfate; and the dewatering properties of the solids generated. Of particular concern in the pilot plant work were the effects of sulfate concentration in the feed liquor and the extent of absorbent regeneration (reactor pH) on the reactor performance.

The composition of the spent scrubber solution (simulated and actual) fed to the regeneration system varied over the following ranges:

$$[Na^+_{active}] = 0.25\text{-}2.30M$$

$$[SO_4^=] = 0.05\text{-}1.70M$$

$$pH = 5.7\text{-}6.6$$

Most of the runs were made with active sodium levels between 0.40M and 0.55M and sulfate levels up to 1.0M. However, a number of runs, particularly closed-loop, were made at high active sodium (and sulfate) concentrations. These runs were designed primarily to examine the effects of high TDS (total dissolved solids) levels on oxidation in the scrubber system and of high TOS (total oxidizable sulfur) levels on sulfate precipitation.

The nominal reactor system operating conditions and solution compositions examined are listed in Table IV-2. In all cases, the reactor vessels were open-top, baffled tanks (four baffles). Single propeller-type agitators were used for mixing. Stirrer speeds generally ranged from 200 rpm to 300 rpm.

TABLE IV-2

SUMMARY OF NOMINAL REACTOR OPERATING CONDITIONS

General Conditions:
Temperature = 105-140°F
Agitation = Propeller (200-300 rpm)
$Ca(OH)_2$ Feed = Dry Solids

$[Na^+_{active}]$	$[SO_4^=]$	Type	Nominal Holdup	Extent of Regeneration (Reactor Effluent pH)
0.25M	0.8M	CSTR	30 mins.	7.5
0.45-0.55	0.05	CSTR	30	7.5
	0.5	CSTR	30	8.0
	0.6	CSTR	30	7.5 & 12
	0.6	CSTR	6.0	7.5 & 12
	0.75	CSTR	30	12 & 12.5
	0.8	CSTR	30	7.5, 11 & 12.5
	0.8	ADL	5 & 50	12
	0.9-1.0	CSTR	30	8 & 11.5
2.0	0.25	CSTR	30	12
	1.6	CSTR	10-15	7.5 & 11

a. Calcium Utilization

Calcium utilizations in runs with both reactor systems were high -- generally greater than 95% of the available $Ca(OH)_2$ in the lime feed. There appeared to be no effect of reactor configuration (ADL versus CSTR) on the utilization of calcium, nor was any effect of sulfate concentration on calcium utilization observed over the range of conditions studied. (In testing prior to this program, though, utilization was found to decrease slightly at very high sulfate levels.) There was, however, a slight dependence of utilization on reactor operating pH and on reactor holdup time.

In the pH range 7.4-11.0, calcium utilizations generally approached, and sometimes exceeded, 100% of the available $Ca(OH)_2$ for reactor holdup times from 25 minutes to 60 minutes. Utilizations in excess of 100% can be attributed to a number of factors including variations in the lime feed composition and analytical errors, as well as the reaction of a portion of the calcium value normally considered to be unavailable at high pH levels (e.g., $CaCO_3$). The average utilization observed in all runs below a pH of 11.5 was 98.5% ± 3% of the available $Ca(OH)_2$, as determined from the analysis of the reactor effluent solids. This would be roughly equivalent to utilization of 94-95% of the total calcium in the raw lime.

At pH levels of 11.5-12.5, the average utilization dropped off slightly to 96% ± 1% of the available $Ca(OH)_2$ (or 91-92% of the total calcium value). During continuous closed-loop operations at reactor pH's greater than 11.0 and with a reactor holdup of 25-30 minutes, the thickener overflow and filtrate were observed to have slightly higher pH levels than the reactor effluent. This increase in pH, on the order of 0.2 pH units (confirmed by slightly higher OH^- concentrations), indicated that the reactor effluent at the shorter residence times was not quite at equilibrium and that some additional reaction was occurring in the thickener. Regeneration to a pH above 8 required a holdup time greater than 20 minutes for essentially complete reaction.

b. Effluent Soluble Calcium Concentrations

Soluble calcium concentrations in the reactor and thickener overflow liquors varied inversely with sulfite concentration, as would be expected, and were apparently independent of reactor type (ADL versus CSTR) and reator holdup time (30 minutes versus 60 minutes). The measured ranges of soluble calcium concentrations are summarized in Table IV-3.

At all but the lowest active sodium levels (0.08-0.13M $SO_3^=$), soluble calcium concentrations were well below 100 ppm. At these levels, there was no evidence of scale buildup in the scrubber system during closed-loop operations. However, in one run at the lowest active sodium concentrations (approaching dilute mode conditions), soluble calcium levels exceeded 500 ppm and there was some buildup of calcium sulfite and carbonate in the tray tower resulting in an increase in the pressure drop across the tower (trays plus demister) from 4 inches to 6 inches H_2O over the course of four days of closed-loop operation. The high calcium levels and solids deposition

TABLE IV-3

SUMMARY OF SOLUBLE CALCIUM CONCENTRATIONS

Reactor Type (Total Holdup)	$[Na^{+}_{active}]$	$[SO_4^{=}]$	Ionic Strength μ	$[Ca^{++}]$
CSTR (10 mins.)	0.23M	0.08-0.13M	$\sim$ 2.8	600-800 ppm
CSTR & ADL (30 & 60 mins.)	0.4-0.55	0.2-0.3	2.2-4.0	25-95
CSTR (15 & 30 mins.)	1.7-2.3	0.7-0.9	5.2-8.2	15-30

suggest significant supersaturation with respect to calcium sulfite, similar to that experienced at low sulfite concentrations in the dilute mode testing (see Chapter VII).

In Figure IV-5 the product of the soluble calcium and sulfite concentrations is plotted against the apparent solubility product curve predicted by the method of Kusik and Meissner.[7] All the experimental solubility product data for both the thickener overflow and reactor effluent fall above the predicted curve. In general the measured calcium concentrations and experimental solubility product data for the thickener overflow tend to be slightly lower than those for the reactor effluent. There are a number of periods, though, during closed-loop operations when thickener overflow calcium values and concentration products were equal to or slightly greater than reactor effluent levels.

It would be anticipated that at steady-state, thickener overflow values would be lower than reactor effluent values. First, the holdup time in the thickener ranged from six to ten hours in the closed-loop runs, allowing considerable time for desupersaturation. Second, and perhaps more important, the thickener overflow was diluted by the addition of filter wash water. In the case of intermediate active sodium levels this tended to decrease total solubles concentrations on the average by about 5%; however, at the higher active sodium levels, this decreased solubles levels by an average of about 25% (due to the lower feed forward rates). Thus, the experimental solubility products in the thickener overflow at the higher active sodium levels appear closer to the predicted curve, and should, at most, represent saturation levels for the indicated solutions.

These results suggest that the degree of supersaturation indicated by the difference between the predicted curve and experimental data may be an artifact or an overstatement of any actual level of supersaturation. There are two possible explanations for the apparent supersaturation levels. First, the predicted curve may be slightly low, a conclusion independently reached from dilute mode data (Chapter VII). The relationship was calculated based upon literature data for low ionic strengths using the method formulated by Kusik and Meissner for calculating activity coefficients at high ionic strengths. The method is only good to about 10-20% and any error in the data base would be translated directly into the predicted curve. Second, the $CaSO_3 \cdot 1/2H_2O$ solubility product curve may not apply to the product solids where there is an appreciable degree of sulfate precipitation. The calcium sulfite/sulfate solids may be present as a mixed crystal, which could have a different solubility product.

Based upon the system operation in closed-loop, as long as soluble calcium levels are in the range of or below 100 ppm, there is no potential for scale formation in the scrubber system. Even if a small amount of supersaturation exists at these low levels (at most, 50 ppm Ca^{++}), the tendency in the scrubber system is to increase the solubility of calcium by conversion of sulfite to sulfate and bisulfite.

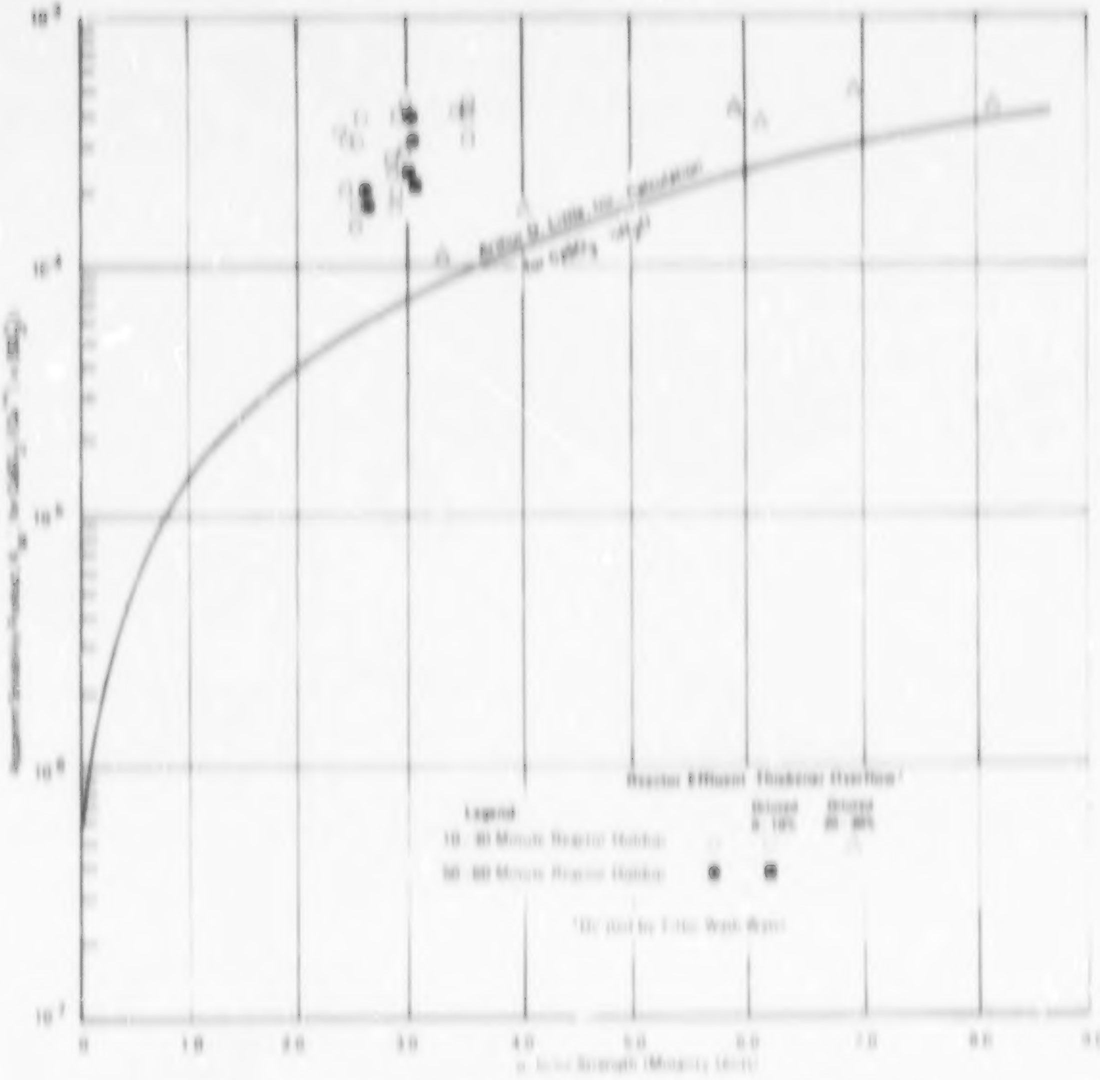


FIGURE IV-5 RELATION OF OBSERVED APPARENT SOLUBILITY PRODUCTS TO SATURATION VALUES FOR $CaSO_3$ REGENERATION WITH LIME

c. Precipitation of Calcium Sulfate

A careful analysis of the solids produced show that a significant amount of calcium sulfate precipitation occurs over a wide range of soluble sulfate concentration. The amount of calcium sulfate precipitated was found to be strongly a function of the soluble TOS and sulfate concentrations. The sulfate dependence is shown in Figure IV-6, in which observed molar ratios of ($CaSO_4/CaSO_x$) in the reactor effluent solids, corrected for the small amount of occluded or entrained Na_2SO_4, are plotted against sulfate concentration in the feed liquor for TOS levels in the range of 0.4-0.5M. The general relationship indicated by the dashed line agrees quite closely with that developed from the laboratory program for the same TOS range.

Figure IV-7 shows a general correlation plot of sulfate precipitation measured in all laboratory and pilot plant runs over the entire range of liquor compositions tested in the concentrated mode. Here, the molar ratio of calcium sulfate-to-calcium sulfite is plotted as a function of the soluble sulfate-to-sulfite ratio in the reactor bleed liquor. A number of other possible relationships were tested covering different ratios (and powers) of concentrations in both the feed and bleed liquor in order to establish a reasonable correlation. The simple relationship shown in Figure IV-7 provides the closest correlation -- one which is also intuitively reasonable.

It should be pointed out that Figure IV-7 applies only to concentrated-mode operations. In dilute mode operations the sulfate solubility product is exceeded and the ratio of sulfate to sulfite in the product solids is governed by the solubility products of hydrated lime and gypsum, and by the amount of sulfite that must be precipitated prior to reaching the gypsum solubility product (see Chapter VII).

The relationship shown in Figure IV-7 can be expressed as follows:

$$\left(\frac{\text{mols } CaSO_4}{\text{mol } CaSO_3}\right)_{\substack{\text{reactor}\\ \text{solids}}} = 0.0365 \left(\frac{[SO_4^=]}{[SO_3^=]}\right)_{\substack{\text{reactor}\\ \text{liquor}}} \qquad (1)$$

or,

$$\left(\frac{\text{mols } CaSO_4}{\text{mol } CaSO_x}\right)_{\substack{\text{reactor}\\ \text{solids}}} = \frac{0.0365([SO_4^=]/[SO_3^=])_{\text{reactor liquor}}}{1 + 0.0365([SO_4^=]/[SO_3^=])_{\text{reactor liquor}}} \qquad (1A)$$

In this relationship calcium sulfate precipitation is inversely proportional to sulfite concentration which suggests that the greatest amount of sulfate can be precipitated when sulfite concentration is at a minimum -- that is, when the scrubber bleed liquor is only partially neutralized or when

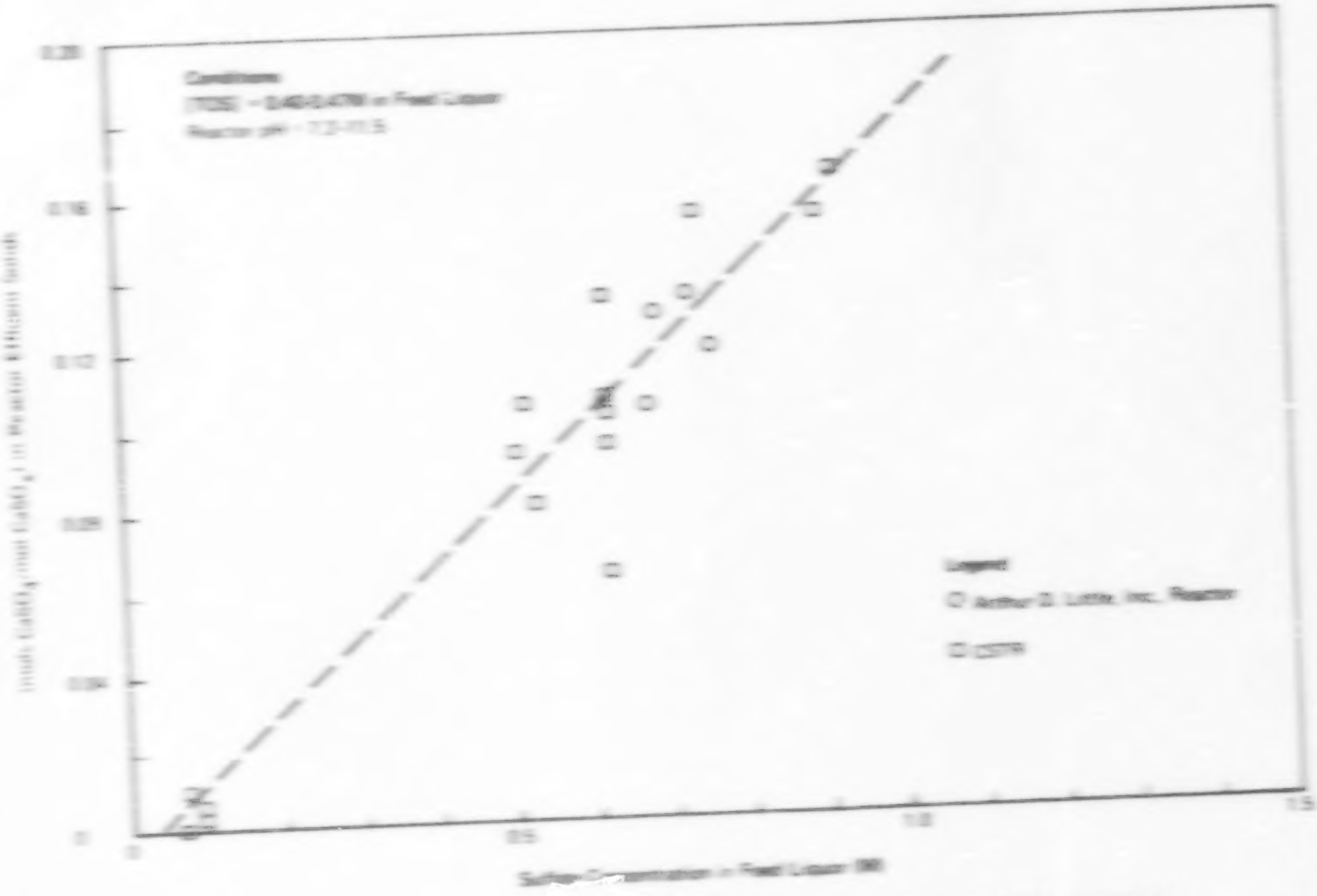


FIGURE IV-6 ($CaSO_4$/$CaSO_3$) RATIO IN REACTOR SOLIDS AS A FUNCTION OF SULFATE CONCENTRATION — LIME REGENERATION

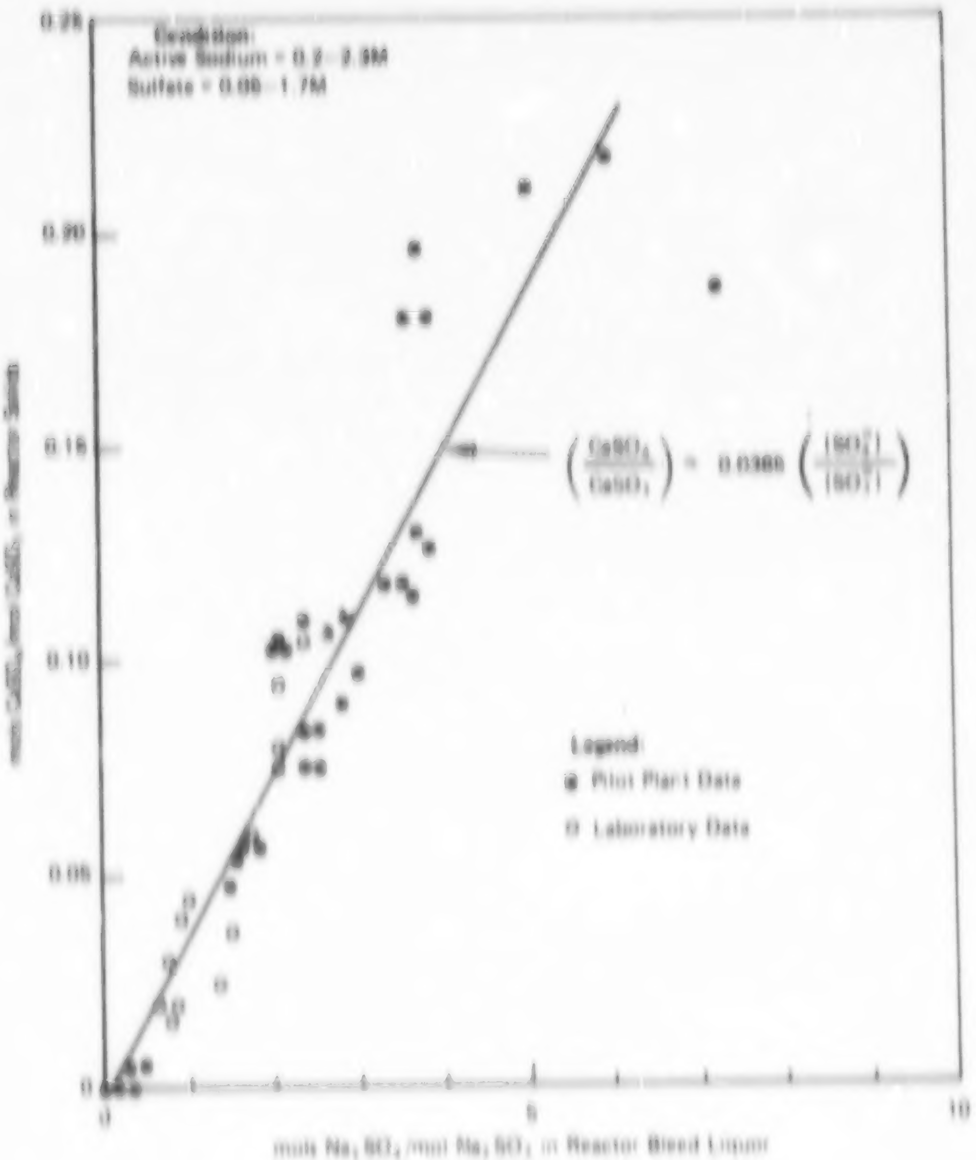


FIGURE IV-7 $(CaSO_4/CaSO_3)$ RATIO IN REACTOR SOLIDS AS A FUNCTION OF REACTOR LIQUOR COMPOSITION the regeneration reaction is carried out to a relatively high pH (where little sulfite exists). Laboratory data on the effect of the extent of regeneration on sulfate precipitation, as discussed previously, do reflect such a "U"-shaped curve.

While equations (1) and (14) can be used to predict the amount of sulfate that can be precipitated, and thereby the amount of oxidation that can be tolerated, laboratory data on the stability of the calcium sulfate precipitated indicate that some redissolution of the calcium sulfate may occur by continual intimate contacting of the solids with the mother liquor. It would be expected then, that some calcium sulfate redissolution together with additional calcium sulfite precipitation would occur in the dewatering system. No such redissolution could be substantiated in the pilot plant operations; however, a small amount of redissolution was observed in the prototype system at Gulf Power Company's Scholz Steam Plant (see Volume III). During one period of extended operation of the prototype system under stable conditions, the reactor solids contained an average molar ratio of calcium sulfate to total calcium sulfur salts of 0.13, while the filter cake ran 0.110-0.115. This corresponds to a 10-15% reduction in the amount of calcium sulfate across the dewatering system.

Applying this redissolution factor (assuming that it holds over all sulfate precipitation rates), equation (14) becomes:

$$\left(\frac{\text{mole CaSO}_4}{\text{mol CaSO}_x}\right)_{\text{cake}} = \frac{0.032([\text{SO}_4^=]/[\text{SO}_3^=])_{\text{reactor liquor}}}{1 + 0.0365([\text{SO}_4^=]/[\text{SO}_3^=])_{\text{reactor liquor}}} \qquad (15)$$

This equation can be used in conjunction with estimated sodium losses (occluded in the filter cake) to predict the concentrations of sodium sulfate and sulfite required to keep up with given levels of oxidation. For example, assuming that no sodium salts are lost in the cake, a mol ratio of $CaSO_4$ in the cake to total calcium-sulfur salts of 0.15 would be required to keep up with a total system oxidation rate of 15% (0.15 mole $SO_3^=$ oxidized/mol SO_2 absorbed). According to equation (15) above, such a calcium sulfate precipitation rate would require a molar ratio of sulfate-to-sulfite of 5.65 in the regenerated liquor. That is, to maintain an active sodium concentration of 0.5M Na^+ with 0.2M as sodium sulfite, the sodium sulfate concentration at steady-state would be about 1.13M.

In actuality, the steady-state sodium sulfate level would be slightly lower than 1.13M because some sodium sulfate is lost in the occluded liquor with the filter cake. This reduces the required calcium sulfate precipitation. For the same oxidation rate of 15% used in the previous example, but with 3.5% of the dry cake weight as sodium salts (2.0% as sodium sulfate), the required ratio of calcium sulfate to total calcium-sulfur salts drops to 0.135. This would decrease the necessary ratio of sulfate-to-sulfite in the liquor from 5.65 to 5.0; so, for the same 0.2M sulfite level, the sulfate concentration would only reach 1.0M at steady-state.

Normally, the system chemistry would self-adjust to the sulfate/active sodium level required to sustain the rate of oxidation being experienced. The system would simply be charged to a total sodium concentration consistent with the minimum desired active sodium concentration and the maximum rate of oxidation anticipated. There is evidence, though, from prior pilot plant work at ADL and operation of the prototype system that the maximum amount of sulfate that can be precipitated simultaneously with calcium sulfite may be limited to 25-30% of the total calcium-sulfur salts. Also, as will be discussed later, solids properties deteriorate with increasing sulfate content of the solids. This alone may limit tolerable oxidation rates to about 25% of the SO_2 absorbed.

It is possible to reduce oxidation by increasing total dissolved solids levels (see Chapter III). Ultimately, though, allowable operating concentrations will be limited by the solubilities of the sodium salts, since at very high TDS levels it may still not be possible to precipitate sufficient calcium sulfate without exceeding sodium salt solubility limits. At the equivalent of 0.9M sulfite concentration (~2M active sodium including bisulfite or hydroxide), a 1.3M sulfate level or higher will be required to keep up with an oxidation rate of only 4-5%. Taking into consideration the presence of a minimal amount of sodium chloride, such a liquor would have a sodium sulfate saturation temperature of 75-85°F. At such concentrations of active sodium, either the tanks and lines must be heated (particularly during shutdown), or else sodium salts must be intentionally purged in the filter cake to maintain lower sulfate levels.

d. Dewatering Properties of Solids

Although the relative performance of the ADL two-stage reactor and the CSTR were found to be comparable with regard to calcium utilization, effluent soluble calcium concentrations, and precipitation of calcium sulfate, there was a noticeable difference in the quality of solids produced. In prior testing and during the EPA program the two-stage reactor demonstrated a capability for operating over a much wider range of system conditions (pH and sulfate concentration) than the CSTR with respect to the production of waste solids with acceptable settling and filtration properties.

Two parameters are used in characterizing the solids settling properties: the bulk or initial settling rate, and the density (solids content) of the settled solids. The settling rate is primarily a measure of the crystal size (and, to some degree, crystal shape) and is used along with the compaction time in sizing the thickener. However, both the settling rate and compaction time are partly a function of the slurry concentration and, therefore, are not necessarily a direct measure of the quality of the solids. The density of the settled solids is primarily dependent on the crystalline form and is a measure of the slurry concentration that can be achieved in the thickener underflow. The density of the settled solids is a better indication of the filterability than is the settling rate, since it is a measure of how well particles compact under the force of gravity. These settling parameters are determined for the reactor product slurry by measuring the rate of fall of the meniscus (slurry/clear liquor interface) in a graduated cylinder, as described in Appendix C.

The filterability of the solids is characterized by the insoluble solids content of the filter cake and by the ease with which the occluded sodium salts in the mother liquor can be washed from the cake. These are used rather than filtration rate, since it is of principal importance to produce a material with good handling properties and with minimal environmental impact rather than simply to minimize filter size.

Comparative Dewatering Properties

The effects of reactor holdup and operating pH on the solids generated in the CSTR were initially studied in the preliminary, open-loop reactor tests using settling rate and the density of settled solids to characterize the quality of the solids.

Table IV-4 shows the effect of reactor operating pH on the quality of solids produced in a CSTR with a feed liquor containing 0.6M sulfate and 0.46M TOS. The quality of the solids produced at a pH of 7.5 was good at both 30 minute and 60 minute reactor holdup times. As pH was increased to 12.0, the quality of the solids deteriorated as shown by the marked decrease in the solids settling rates and in the densities (wt % solids) of the settled solids. This pH effect was much more pronounced for the 60 minute holdup than for the 30 minute holdup; however, in neither case was the loss of solids properties irreversible. Returning the pH to a low level resulted in a return to acceptable solids. In light of the greater sensitivity of the 60 minute reactor holdup, the shorter 30 minute holdup provides a more reliable design basis for a CSTR. Regeneration to a pH above 8 required a holdup time greater than 20 minutes to achieve good utilization of lime.

The effect of sulfate concentration on solids properties over a range of pH for the 30 minute CSTR (in both open- and closed-loop runs) is shown in Table IV-5. Increasing sulfate levels results in poorer solids, an effect which is aggravated by high pH. The observed decrease in settling rates is indicative of smaller particle sizes, and the lower densities of the settled, partially compacted solids implies a change in the form of the crystal agglomerates generated. Electron microscopy and optical studies of the solids confirm the difference in the crystals. As shown in Figure IV-8, the poorer settling solids are generally made up of smaller particle sizes with more needle-like crystal structures, while the solids with good settling properties are agglomerates of needles.

These differences in settling properties are also reflected in the filterability of the solids. In general, low settling rates and low densities of settled solids are consistent with low solids content in the filter cake and poor wash efficiencies. However, it should be noted that as suspended solids levels in the reactor effluent increase, settling rates generally decrease (settling becomes "hindered") and the density of the settled solids increases because of the higher compaction force.

TABLE IV-4

EFFECT OF CSTR pH AND HOLDUP TIME ON SOLIDS PROPERTIES

General Reactor Conditions: Reactant Feed - Dry $Ca(OH)_2$
Reactor Temperature - 105-115°F
Agitation Rate - 200-250 rpm
Liquor Feed Composition - [TOS] = 0.40M
$[SO_4^=]$ = 0.60M
pH = 5.8

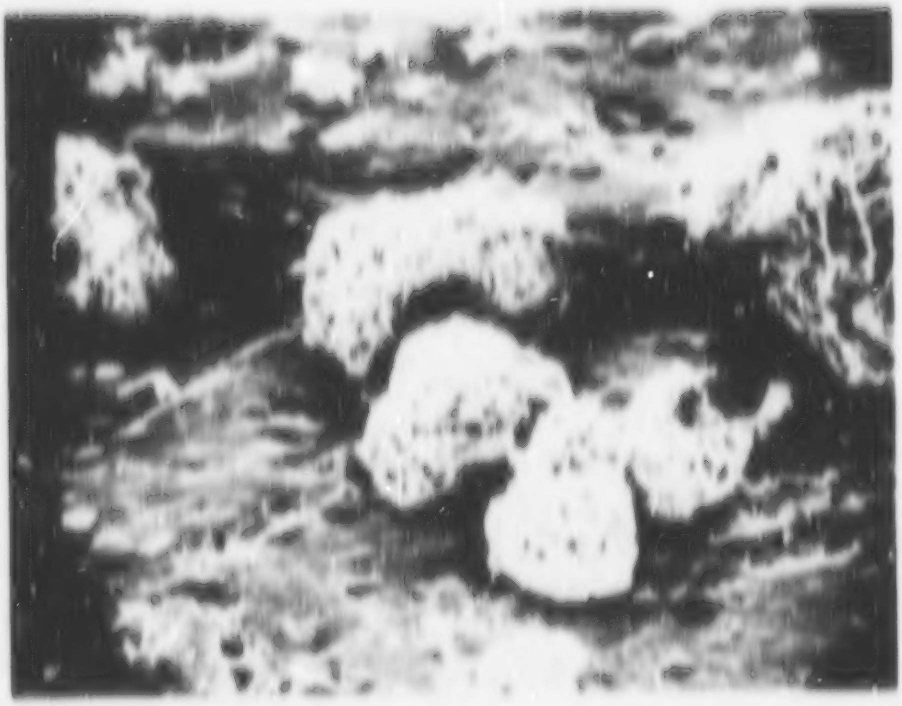
Reactor Holdup (mins.)	Reactor Effluent		Solids Settling Properties	
	pH	Approximate Suspended Solids (gms/l)	Bulk Settling Rate (ft/min.)	Wt % Insolubles in Settled Solids (2-3 hrs.)
60	7.2-7.4	30	0.20-0.23	26-36
	12.0	55	0.05	6
30	7.5	35	0.20-0.25	26
	11.9	50	0.15-0.20	15

TABLE IV-3

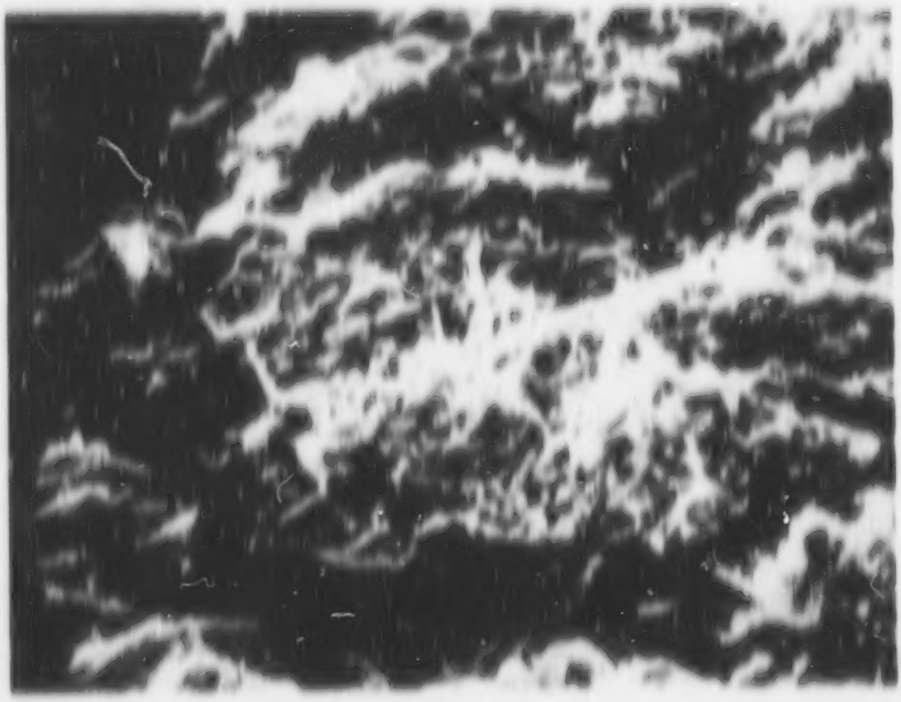
EFFECTS OF SULFATE CONCENTRATION AND pH ON SETTLING PROPERTIES OF SOLIDS PRODUCED IN A CSTR WITH A 30 MINUTE HOLDUP

General Reactor Conditions:
Reactor Holdup - 30 mins.
Reactant Feed - Dry $Ca(OH)_2$
Reactor Temperature - 105-120°F
Agitation Rate - 250-350 rpm
Liquor Feed Composition - [TDS] = 0.45-0.55M
pH = 5.8

Reactor Feed		Reactor Effluent		Solids Settling Properties	
[TDS]	Feed [$SO_4^=$]	Approximate pH	Suspended Solids (gms/l)	Bulk Settling Rate (ft/min.)	Approximate wt % Insolubles in Settled Solids (2-3 hrs.)
0.45-0.55M	0.25M	7.5	30	0.25-0.30	45
	0.5	7.5-8.5	30	0.20-0.25	25
	0.6	7-8	30	0.15-0.25	20-25
		11.9	50	0.15-0.20	15
	0.75	12.0	50	0.05-0.10	15-20
		12.5	50	0.05-0.10	10-12
	0.8	11-11.5	20	0.10-0.15	10
	0.9-1.0	9-10	25	<0.05	5-15
		11.5-12.0	25	<0.05	5
1.7-2.3	0.25	12.0	-	0.03	5-10
	1.5-1.7	7-8	60	0.08	25-30
		12.2	65	0.02	10



AGGLOMERATES CHARACTERISTIC OF GOOD SETTLING SOLIDS



NEEDLE-LIKE CRYSTALS CHARACTERISTIC OF POOR SETTLING SOLIDS

FIGURE III-5 SCANNING ELECTRON MICROGRAPHS OF SOLIDS

Table IV-6 compares the settling and filtration characteristics for solids produced in the concentrated lime mode using both the ADL reactor and the CSTR. These results show that the density of the compacted solids, rather than the initial settling rate, is a better indication of the filterability and washability of the solids.

The data presented in Table IV-6 show that both reactors are capable of producing solids with good dewatering properties, and that in both reactors the solids properties deteriorate with increasing sulfate concentration. However, the CSTR is more sensitive than the ADL reactor to sulfate concentration and pH. Solids generated in the CSTR at high pH and sulfate concentration do not settle or filter as well as those obtained in the ADL reactor under equivalent conditions. This difference is shown in Figure IV-9, a plot of filter cake solids content versus sulfate concentration at intermediate TOS levels. Since only limited testing with the two-stage (ADL) reactor was performed during the EPA program, the data shown in Figure IV-9 include results obtained with the ADL reactor in prior work. At solids contents above about 45% the filter cake is much like a moist powder. At solids contents below 40%, the cake is wet and relatively easily liquefied.

The effect of sulfate concentration appears to be dampened by increasing TOS (active sodium) levels as indicated by the data presented in Tables IV-5 and IV-6. This suggests that the effect of sulfate is primarily one of slowing the reaction rate. Increasing TOS levels results in an increase in reaction rate, as indicated by the short holdup times required to achieve good utilization.

It is evident, therefore, that the quality of the filter cake produced is not a function of the sulfate concentration alone, but rather a function of the ratio of sulfate and sulfite concentrations. This relationship is shown in Figure IV-10, in which the solids content of filter cakes produced in closed-loop runs is plotted against the ratio of sulfate-to-sulfite concentrations in the regenerated liquor for the range of solution compositions tested (and the equivalent rates of oxidation that can be handled as indicated by the solids analyses or as derived from Figure IV-7). As shown, the multistage reactor results in a filter cake with solids contents (insoluble solids) greater than 40% at oxidation rates as high as 20% of the SO_2 absorbed; while the filter cake produced using a CSTR for absorbent regeneration falls below 40% solids content at oxidation rates of between 10% and 15% of the SO_2 absorbed.

Filter Testing (Washability)

The lowest level of solubles attained in the concentrated active sodium mode in continuous, closed-loop operations was about 1.7 wt % solubles (dry cake basis). This was achieved in a run at active sodium concentration of 0.4M using slightly more than three displacement washes sprayed onto the cake with two full-cone nozzles in series. As indicated in Table IV-6, the reduction in soluble solids in the cake is a function of three variables: dissolved solids levels in the mother liquor; the number of displacement washes; and the quality (solids content) of the filter cake.

TABLE IV-[illegible]

COMPARATIVE SETTLING AND FILTRATION PROPERTIES[a]

TSS Level (%)	Reactor Source Type-Holdup (min.)	[illegible]	pH	[illegible][b]	Settling Properties: Bulk Settling Rate (ft/min.)	Settling Properties: Wt % Insolubles in Settled Solids (2-3 hrs.)	Filter Cake Solids: Wt % Insolubles	Filter Cake Solids: Wt % Solubles (dry basis)	Filter Cake Washability: Approximate No. of Displacement Washes[c] (spray type)[d]	Filter Cake Washability: % Reduction of Solubles	Filter Cake Washability: % Reduction Displacement Washes
[illegible]	[illegible]	[illegible]	11.5-12	[illegible]	0.22	—	52	1.5	1.5 (2 PC)	85	[illegible]
	[illegible]	[illegible]	9-12	[illegible]	0.20	25	48	3-4	1.5 (1 PC)	[illegible]	[illegible]
	[illegible]	[illegible]	11.5-12	[illegible]	0.25	20	40	4	1.0 (1 PC)	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	0.22	25	40	1.3-2.5	1.1 (2 PC)	[illegible]	[illegible]
	[illegible]	[illegible]	7-8	[illegible]	0.25	20	[illegible]	2.5-4	2.5-3.5 (2 PC)	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	0.22	10	35	[illegible]	2.3 (1 PC)	[illegible]	[illegible]
	[illegible]	[illegible]	8-9	[illegible]	0.07	5	22	[illegible]	1.4 (1 PC)	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.08	25-30	50	1.5	4.0 (3 PC)	90	[illegible]

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[a] [illegible]

[b] [illegible]

[c] [illegible]

[d] [illegible]

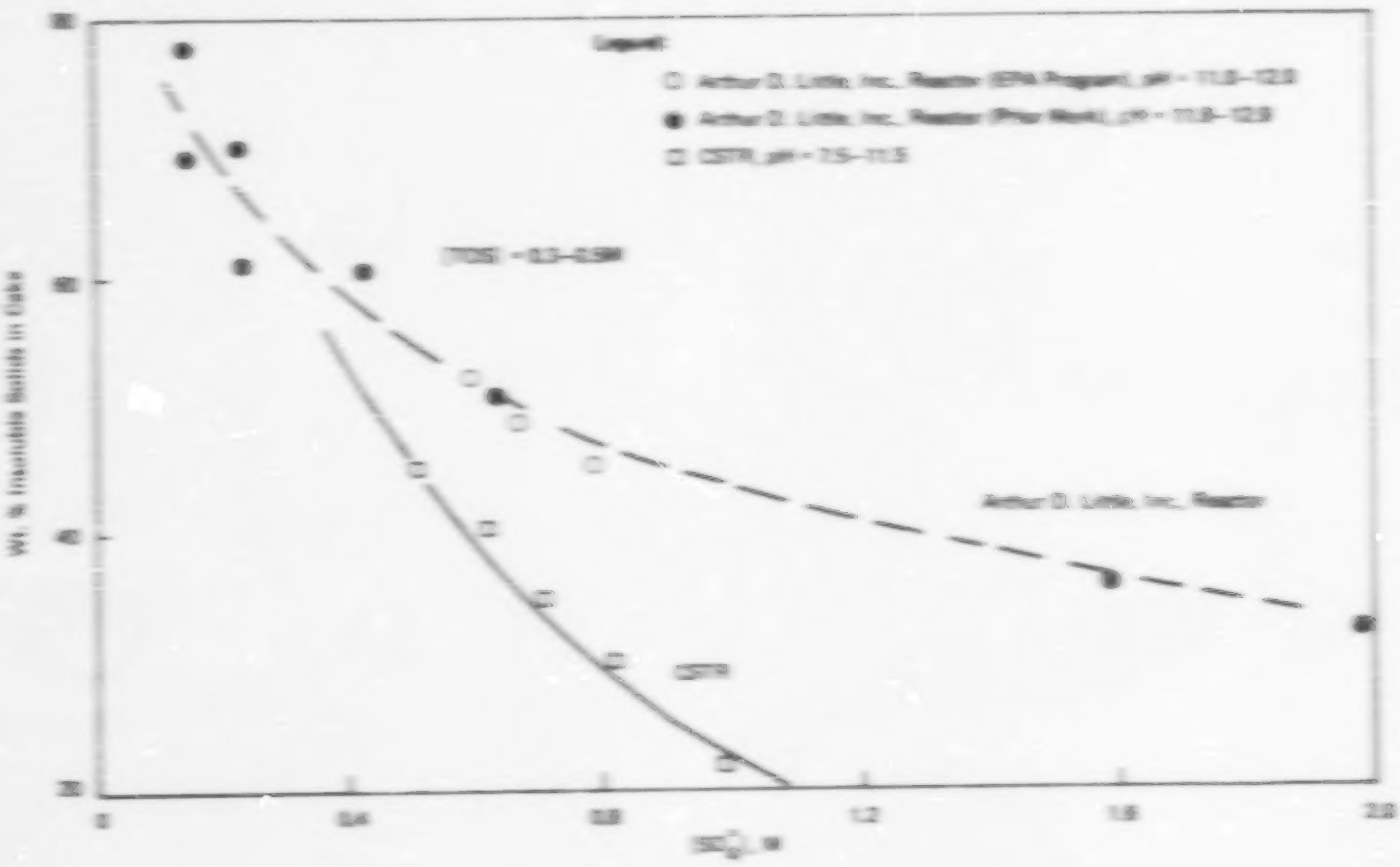
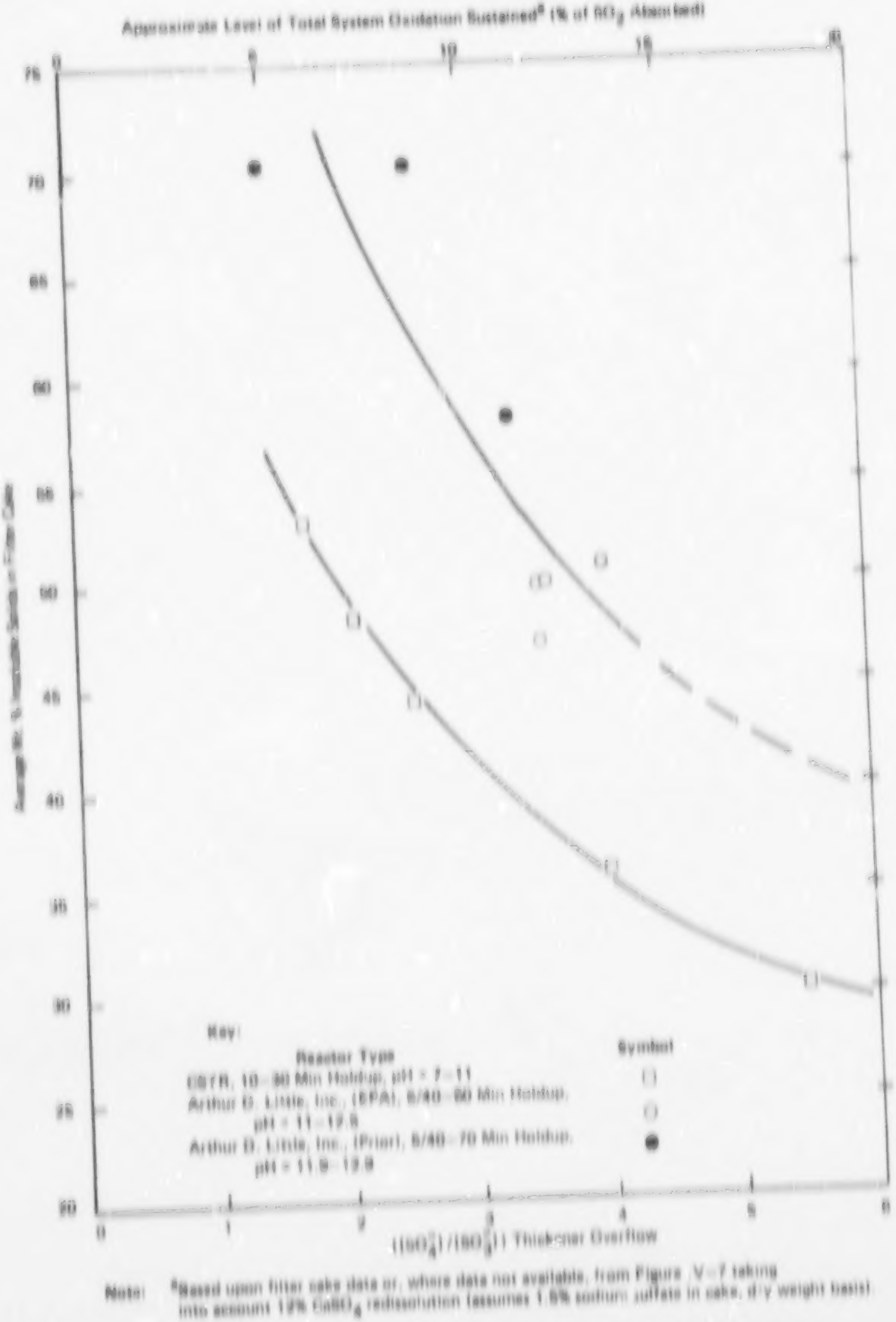


FIGURE IV-8 AVERAGE WT. % INSOLUBLES IN FILTER CAKE VERSUS SOLUBLE SULFATE CONCENTRATION – INTERMEDIATE SODIUM CONCENTRATION/LIME REGENERATION



Note: ^{a}Based upon filter cake data or, where data not available, from Figure IV–7 taking into account 12% $CaSO_4$ redissolution (assumes 1.5% sodium sulfate in cake, dry weight basis).

FIGURE IV–10 SOLIDS CONTENT OF THE FILTER CAKE AS A FUNCTION OF SYSTEM OXIDATION

The practical minimum solubles level that can be achieved was determined in a special set of tests conducted with the pilot plant filter. The purpose of these tests was not only to determine washability but also to evaluate the effects of filter control variables on filtration rate. The testing was done using fresh solids produced in the ADL reactor at 0.4M active sodium and 0.6M sulfate.

These tests demonstrated that the cake can be realistically washed to a level of 1.2-1.5 wt % soluble solids (dry basis), which corresponds to 90% reduction in solubles at 50% solids and the liquor composition tested. The reduction in soluble solids achieved as a function of the number of displacement washes is shown in Figure IV-11. As indicated, about 10% of the occluded sodium salts (almost all of which are sodium sulfate) would leave with the cake regardless of the wash rate unless the cake were repulped. This confirms laboratory data on cake washing. There is apparently a low, but significant, quantity of liquor in the interstices of the crystalline agglomerates, which is not easily washed from the cake. The solubles in this liquor amount to 0.5-1.0% solubles in the cake (dry basis).

As a comparison, the wash data taken during a continuous run at high TDS levels are also plotted in Figure IV-11. At very high wash ratios (eight displacements), the solubles content also approaches 1-2 wt %. However, the number of displacement washes required at these high TDS levels to achieve 2.5 wt % solubles is about five, roughly twice that required at intermediate dissolved solids levels, exceeding the amount of wash water normally available in the process water balance for high-sulfur coal, dual alkali applications.

The maximum cake washing capability for a medium- or high-sulfur coal application would be roughly equivalent to two or three displacement washes (0.6 gpm/Mw for a cake with 50 wt % solids). The number of displacement washes will be limited by the amount of makeup water available for washing as determined by the process water balance and possibly by the operation of the filter. Assuming cake wash behavior similar to that seen in the ADL pilot plant using two sprays in series, 75-85% reduction in soluble solids concentration in the occluded cake liquor can be expected for this level of washing. With a system liquor containing 0.6-0.7M sulfate, 0.5M active sodium, and 0.2M sodium chloride, the resultant solubles in the cake would then be 2-3% (dry cake basis) for a cake containing 50 wt % insoluble solids. To achieve this same level of solubles at high dissolved solids using a wash ratio of 4.5-5 would require roughly 85-100% of the total makeup water available for the system (assuming similar washing behavior as in the pilot plant). Such a large amount of wash water was available in the pilot plant water balance because the lime was fed to the system as dry hydrated lime, not as a slurry; and because the rate of evaporation of water to the gas in the scrubber system was about 30% higher than would be expected in an actual boiler application due to the high flue gas temperatures (saturated gas temperatures of 140-150°F). Even assuming that the same level of sodium losses could be achieved with less water, either by

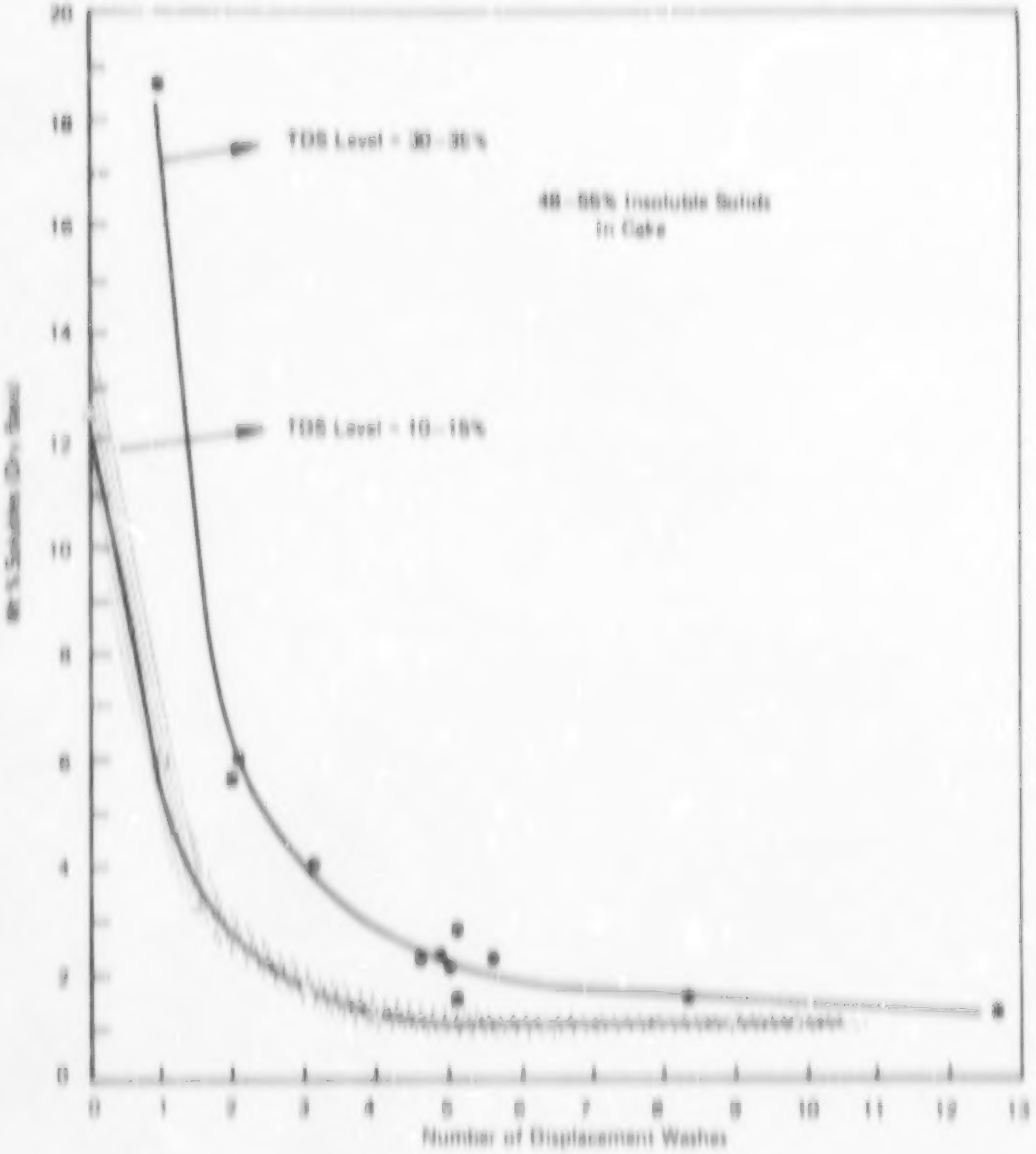


FIGURE IV-11 FILTER CAKE SOLUBLES LOSSES
(TWO OR THREE SPRAYS IN SERIES)

increasing the solids content of the cake to 60-70% solids (which could not be attained in the pilot plant) or by increasing the wash efficiency, the resulting wash water requirements could easily exceed the average rate allowable by the overall system water balance.

The exact amount of solubles loss depends upon a number of factors including dissolved solids levels, the type of wash used (spray configuration), the operating conditions for the filter, and especially the solids properties. The degree of washing that is desirable will also depend in large part on the presence of impurities -- the rate at which they enter the system and the tolerable steady-state impurity levels within the system.

Centrifuge Testing

A six-inch solid bowl centrifuge was tested for comparison with the filter. In general, the centrifuge produced waste solids with 5% to 10% higher solids content (55-65% solids versus 50-55% solids). However, the solids were "masticated" by the centrifuge and were discharged as a much wetter feeling material with considerably poorer handling properties than those of the filter cake. Also, the pilot centrifuge had no provision for cake washing. It is not expected that high sodium recovery efficiency can be achieved using a centrifuge.

e. Sulfite Oxidation in the Reactor System

A significant amount of oxidation occurred in both reactor systems (CSTR's and ADL) in some of the early runs due to use of reactor vessels outside their normal operating capacity (i.e., at very low levels where the propeller agitation caused excessive splashing of the solution). In the initial open- and closed-loop continuous reactor tests, oxidation rates ranged from 0.01-0.30 mole TOS/liter-minute (equivalent to 10 ppm to 280 ppm of SO_2 in the pilot plant system).

Subsequent batch and continuous runs showed that the rate of oxidation was strongly dependent on the degree of agitation, the exposed surface area of the vessel, and the total dissolved solids concentration, indicating that oxidation was primarily a function of gas-liquid contacting. It was found to be essentially independent of sulfite concentration in this concentrated regime, except as it decreased oxygen solubility. Use of proper vessel dimensions (i.e., liquid height-to-diameter ratios of 1:1 and higher) and control of agitation (stirrer speed and impeller size) in later runs reduced oxidation to less than 50 ppm of the SO_2 absorbed. Sealing of the reactor system virtually eliminated oxidation.

1. Summary of Overall System Operation

a. General Operating Conditions

Seven closed-loop, continuous runs were made in the pilot plant in the concentrated active sodium mode using lime for absorbent regeneration. Six of the runs involved a CSTR (10-45 minutes holdup) and one used the

ADL reactor. In addition to the different reactor systems, operating variables included SO_2 inlet concentration (2,400-2,800 ppm and 850 ppm), oxygen content of the flue gas (4-7.5%), active sodium and sulfate concentrations, and the use of both Na_2SO_4 and Na_2CO_3 for sodium makeup. In all runs, hydrated lime was metered to the reactors as a dry solid. General conditions for each run are listed in Table IV-7.

These runs were intended to confirm and extend open-loop data and to test the system operation under a variety of conditions. Although not all process sections were operated under optimal conditions during these runs, the operations did reflect conditions that could be encountered in some process applications. Since much of the data generated during these runs has already been reviewed, the following discussion will be focused on the overall system performance as related to the operating conditions and the performance of each process section.

In each run, the system was primed with liquor of predetermined concentrations and the system operated under a specified set of conditions for three to six days (four to ten system holdup times). Although steady-state operation was not achieved in all runs, sufficient data were collected to characterize the operation of each section for the given set of conditions. The overall system configuration for these closed-loop runs is shown in the process schematic in Figure IV-12.

The scrubber system consisted of the venturi (ΔP = 10-14 inches of water) followed by the tray tower containing two trays. The regenerated liquor was fed directly to the top tray and there was no recycle of any liquor around the tray tower.

b. System Performance Results

Six criteria are used to characterize the system performance:

- SO_2 removal;
- lime utilization;
- oxidation/sulfate control;
- solids properties;
- sodium losses; and
- system reliability and operability (i.e., resistance to upsets, ease of operation, scale potential, and special process problems).

Table IV-8 gives a summary listing of the key results of each of the closed-loop runs. Figures IV-13, IV-14, and IV-15 show schematic process block diagrams for three representative runs -- 402, 404, and 421. These block diagrams express the various system inputs, outputs, and operating characteristics in terms of the SO_2 absorbed.

TABLE IV-7

OPERATING CONDITIONS FOR CLOSED-LOOP OPERATIONS

Scrubber System: Venturi + Two Stages
Venturi ΔP = 12-12.5" H_2O
Venturi L/G = 15-17 gals/Mscf sat'd

Run No.	401	402	403	404	405	421	422
Duration of Run (days)	3.5	4	2.5	3	7	7.5	3.5
Inlet Flue Gas:							
SO_2 (ppm)	2,650	2,400	850	2,800	2,400-2,500	2,400-2,500	2,400-2,500
O_2 (vol. %)	4-5	4-5	4-5	4-5	5	5	7.5
Temperature (°F)	390-410	395-410	395-415	370-390	360-390	380-410	370-390
Reactor System:							
Type	CSTR	ADL	CSTR	CSTR	CSTR	CSTR	CSTR
Holdup (mins.)	40	60	25	30	30	20-25	20-25
Operating pH	7-10	11.5-12	11-11.5	7.5-8.5	7-8 & 11-11.5	7-8[b]	7.5-11.5
Scrubber Operation:							
Absorber L/G (gals/Mscf sat'd - avg)	2.7	2.2	1.4	2.8	2.3	2.35	1.3
Top Tray Feed pH	8-9	11.5-12	11.5-12	7.5-9	7.5-9 & 11-11.5	7-8[b]	8-11.5
Absorber ΔP - 2 Trays + Demister ("H_2O)	3.0-3.5[a]					4.0-4.2	
Absorber Liquor Composition:							
Na^+_{active} (M)	0.55	0.45	0.25	0.45	0.5-0.75	1.8-2.1	1.95-2.1
$SO_4^=$ (M)	1.1	1.8	0.8	0.5	0.7-1.1	1.5-1.7	1.6-1.7
Sodium Makeup Form	Na_2SO_4	Na_2SO_4	Na_2SO_4	Na_2CO_3	Na_2CO_3	Na_2CO_3	Na_2CO_3

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[a] Except in run 405—one tray.

[b] Operation at a pH range of 11-11.5 was examined for a brief period.

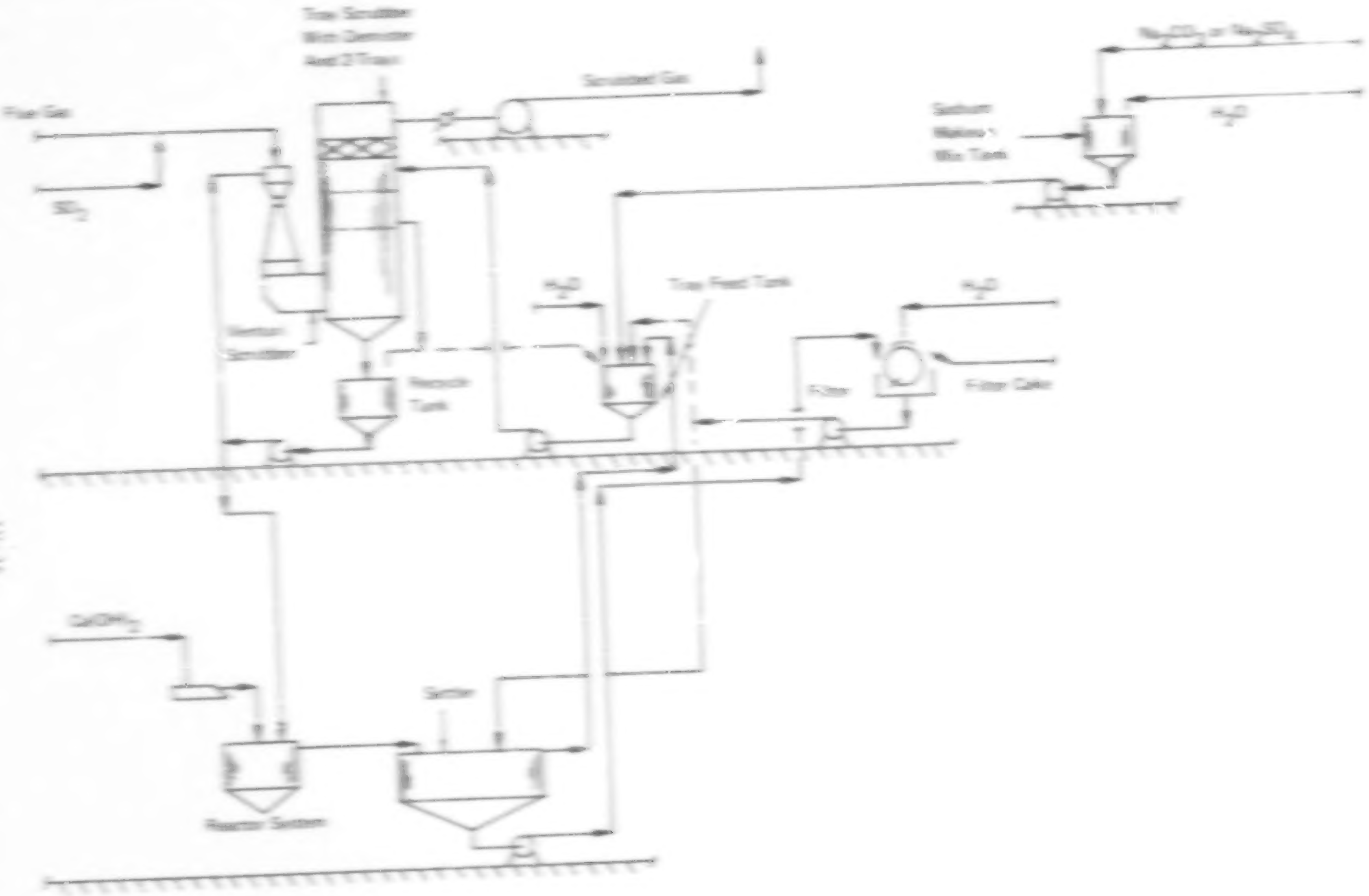
Tray Scrubber
With Demister
And 2 Trays
Scrubbed Gas
Na_2CO_3 or Na_2SO_3
Flue Gas
SO_2
H_2O
Sodium
Makeup
Mix Tank
Venturi
Scrubber
Recycle
Tank
H_2O
Tray Feed Tank
H_2O
Filter
Filter Cake
$Ca(OH)_2$
Settler
Reactor System

FIGURE IV-12 SCHEMATIC FLOW DIAGRAM FOR CONCENTRATED LIME MODE

[illegible]

[illegible]

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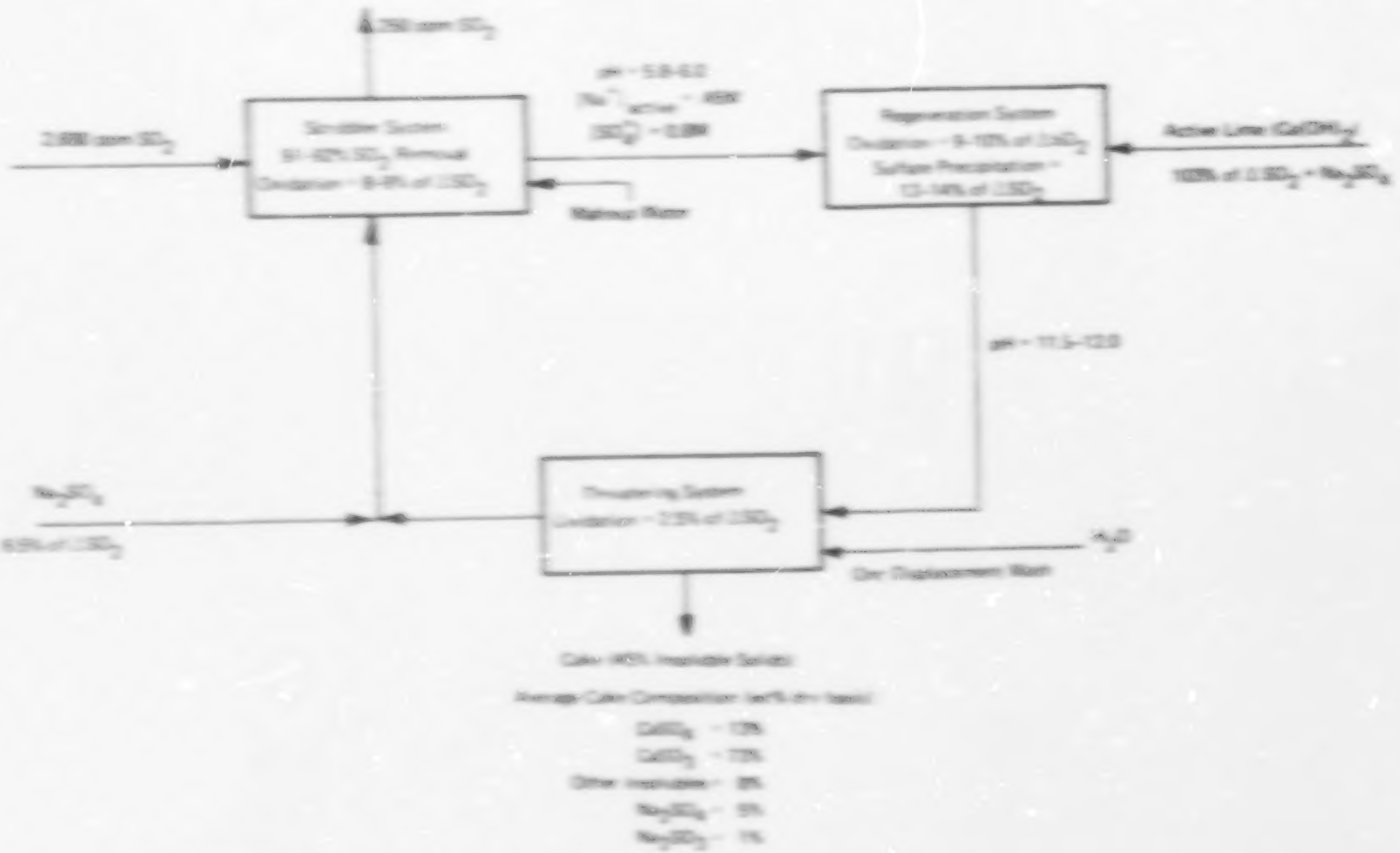
[a] [illegible]

[b] [illegible]

[c] [illegible]

[d] [illegible]



2,800 ppm SO_2
250 ppm SO_2
Scrubber System
91-92% SO_2 Removal
Oxidation ~ 8-9% of ΔSO_2
pH ~ 5.8-6.0
$[Na^+]_{active}$ ~ .45M
$[SO_4^=]$ ~ 0.8M
Makeup Water
Regeneration System
Oxidation ~ 9-10% of ΔSO_2
Sulfate Precipitation ~
13-14% of ΔSO_2
Active Lime $Ca(OH)_2$
100% of ΔSO_2 + Na_2SO_4
pH ~ 11.5-12.0
Na_2SO_4
6.5% of ΔSO_2
Thickening System
Oxidation ~ 2.5% of ΔSO_2
H_2O
One Displacement Wash
Cake (45% Insoluble Solids)
Average Cake Composition (wt% dry basis)
$CaSO_4$ ~ 13%
$CaSO_3$ ~ 73%
Other Insolubles ~ 8%
Na_2SO_4 ~ 5%
Na_2SO_3 ~ 1%

FIGURE IV-12 CONTINUOUS RUN [illegible] – ARTHUR D. LITTLE, INC., REACTOR (Na_2SO_4 MAKEUP)

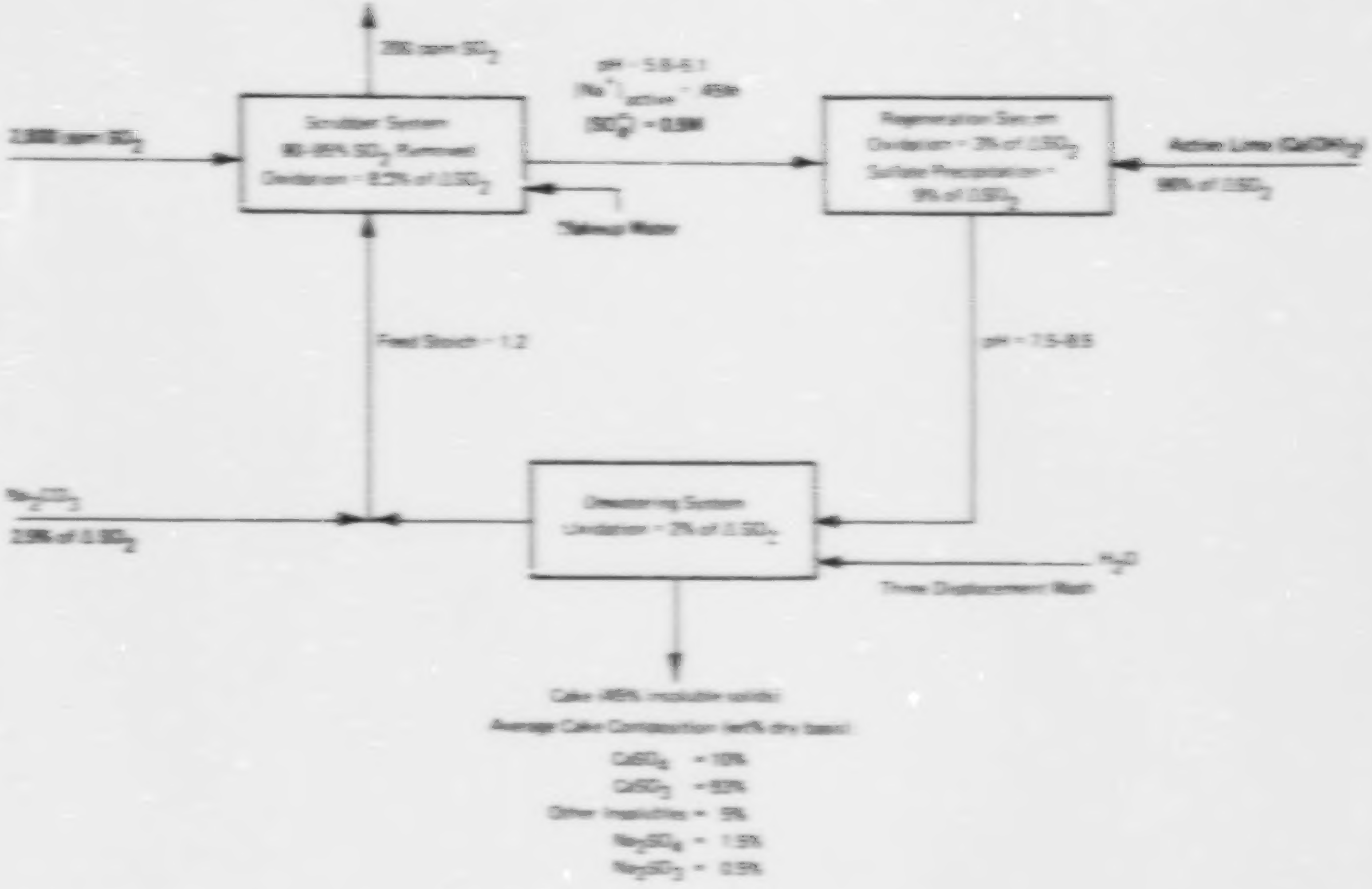

2,000 ppm SO_2
200 ppm SO_2
Scrubber System
90-95% SO_2 Removed
Oxidation = 8.5% of ΔSO_2
Makeup Water
pH = 5.8-6.1
$[Na^+]_{active}$ = 45N
$[SO_4^=]$ = 0.9M
Regeneration System
Oxidation = 3% of ΔSO_2
Sulfate Precipitation = 9% of ΔSO_2
Active Lime ($Ca(OH)_2$)
98% of ΔSO_2
Feed Stoich = 1.2
pH = 7.5-8.5
Na_2CO_3
23% of ΔSO_2
Dewatering System
Oxidation = 2% of ΔSO_2
H_2O
Three Displacement Wash
Cake (45% insoluble solids)
Average Cake Composition (wt% dry basis)
$CaSO_4$ = 10%
$CaSO_3$ = 83%
Other Insolubles = 5%
Na_2SO_4 = 1.5%
Na_2SO_3 = 0.5%

FIGURE IV-18 CONTINUOUS RUN 40A-CSTR REACTOR (Na_2CO_3 MAKEUP)

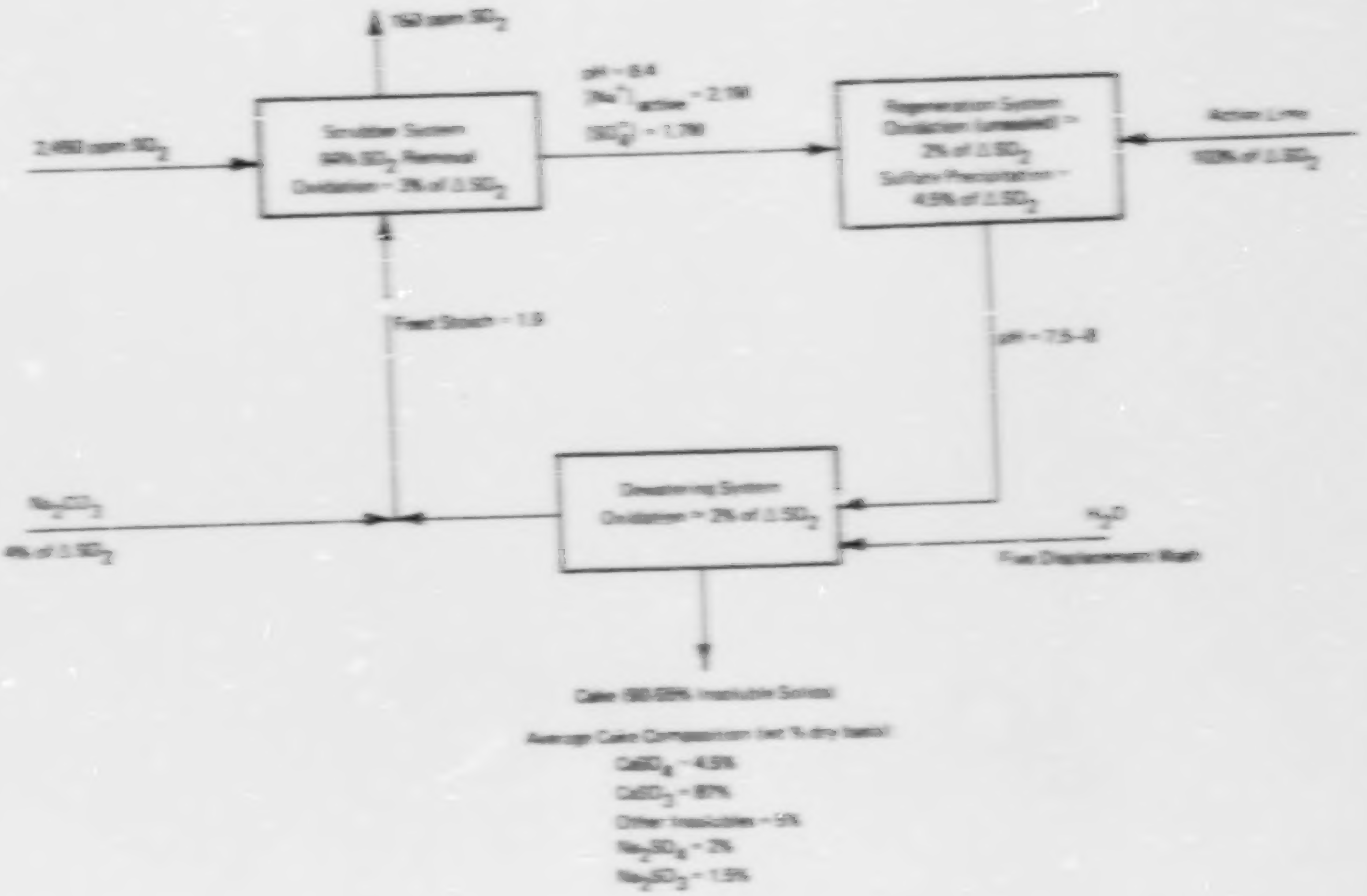

150 ppm SO_2
2,450 ppm SO_2
Scrubber System
94% SO_2 Removal
Oxidation ~ 3% of ΔSO_2
pH ~ 6.4
$[Na^+]_{active}$ ~ 2.1M
$[SO_4^=]$ ~ 1.7M
Regeneration System
Oxidation (unreacted) ~
2% of ΔSO_2
Sulfate Precipitation ~
4.5% of ΔSO_2
Active Lime
103% of ΔSO_2
Feed Stoich ~ 1.9
pH ~ 7.5–8
Na_2CO_3
4% of ΔSO_2
Dewatering System
Oxidation ~ 2% of ΔSO_2
H_2O
Cake Displacement Wash
Cake (50-55% Insoluble Solids)
Average Cake Composition (wt % dry basis)
$CaSO_4$ ~ 4.5%
$CaSO_3$ ~ 87%
Other Insolubles ~ 5%
Na_2SO_4 ~ 2%
Na_2SO_3 ~ 1.5%

FIGURE IV–16 CONTINUOUS RUN 421 – CSTR REACTOR (Na_2CO_3 MAKEUP)

SO_2 Removal

As shown in Table IV-8, there was no difficulty in achieving SO_2 removal rates on the order of 90% and higher in any of the runs. The SO_2 removal rate was primarily a function of the scrubber pH or feed stoichiometry (mols active sodium capacity/mol SO_2 inlet) at which the system was operated. The scrubber bleed pH's shown in Table IV-8 represent the range of operation corresponding to the SO_2 removal efficiencies given. For the most part the scrubber bleed pH's (and removal efficiencies) were maintained in these ranges during the runs.

In the runs at intermediate active sodium concentrations (0.25-0.75M active Na^+), SO_2 removal efficiency varied from 91% at a bleed pH of about 5.8 to 96% at a pH of about 6.2. At the high active sodium levels (runs 421 and 422), slightly higher pH's (or feed stoichiometries) were required to achieve equivalent SO_2 removal efficiencies as in the intermediate active sodium runs. This is attributed to the higher SO_2 equilibrium partial pressures over the more concentrated solutions.

Lime Utilization

In all runs, lime utilization exceeded 93% of the available calcium hydroxide in the raw lime feed. Available calcium hydroxide is measured by titration of the lime with HCl to a phenolphthalein endpoint. In general, the raw lime contained 95-96% calcium (reported as calcium hydroxide) and 91% calcium hydroxide.

The lime feed stoichiometries (mols $Ca(OH)_2$/mol (ΔSO_2 + Na_2SO_4 added)) typically ranged from 0.96 to 1.03, except in run 403, where extremely poor solids properties prevented a reasonable approach to steady-state. In this run, the lime feed stoichiometry was 0.96.

Excluding run 403, the total alkali feed stoichiometries (mols (Na_2CO_3 + $Ca(OH)_2$)/mol (ΔSO_2 + Na_2SO_4 added)) generally ranged from 1.02 to 1.09 during stable operating periods. While these feed stoichiometries are good, it should be pointed out that they are still somewhat greater than would be expected in full-scale operations over extended periods. These were relatively short-term operations (a few days) and sodium makeup rates frequently exceeded sodium losses.

Oxidation and Sulfate Precipitation

The amount of oxidation experienced in the system and the rate of calcium sulfate precipitation differed in each run depending upon the particular set of conditions being tested. The range of total system oxidation examined in the seven closed-loop runs was 7% to 17% of the SO_2 absorbed. Since the system performance at low levels of oxidation (< 10%) is quite good, the closed-loop runs focused on oxidation rates greater than 10%. The one run at 7% oxidation was made at high active sodium concentrations to evaluate sulfate precipitation.

Of importance in these runs is how the system with different types of reactors (ADL versus CSTR) and different active sodium levels performed at the different levels of oxidation, and how the system conditions affected the relative rates of oxidation. As discussed previously (Chapter III), the amount of oxidation experienced in the pilot plant scrubber system (which generally accounts for the majority of the total system oxidation) is higher than that which would be experienced in full-scale systems due to particular pilot plant gas conditions.

Calcium sulfate precipitation has been determined by a careful analysis of the filter cake and reactor effluent solids. Oxidation rates in the scrubber and reactor systems have been determined from material balances around each of these process sections individually. Oxidation rates in the dewatering system (thickener and filter) were determined from overall system balances over a period of at least 24 hours, taking into account changes in inventory within the system and sodium makeup and loss rates. The direct determination of sulfite oxidation in the dewatering system is difficult, since flows are not constant, and wash water and vacuum pump seal water are continually added to the thickener.

The first three runs, 401-403, were made at relatively high rates of oxidation. In runs 401 and 402, total system oxidation ran 18-21% of the SO_2 absorbed primarily because of the high rates of oxidation in the reactor system (which were subsequently reduced by adjusting vessel dimensions and controlling agitation). In run 403, at the same oxygen content in the flue gas but at a low inlet SO_2 level, oxidation totalled 38% of the SO_2 absorbed. In all of these runs, sodium sulfate was used as the makeup source. Therefore, the effective oxidation rates (actual oxidation plus sulfate addition) amounted to 25-27% in runs 401 and 402, and about 40% in run 403.

At these high rates of oxidation, sulfate levels rose to 0.8M and higher in order to precipitate the required amount of calcium sulfate. The CSTR (runs 401 and 403) was not capable of producing solids with good dewatering properties at these high sulfate levels and steady-state operation was not achieved. With the multistage reactor (run 402), on the other hand, reasonably good solids were produced. However, as shown in Figure IV-13, the rate of sulfate precipitation and soluble sulfate losses in the cake (with minimal cake washing) did not quite equal the rate of sulfate additions plus sulfite oxidation, and there was a slight increase in the sulfate-to-active sodium ratio throughout run 402. Assuming the same sodium losses in the cake, this trend would have continued until the sulfate level reached 1.1-1.2M if active sodium were maintained at 0.45M, or until it reached about 0.9M if both the active sodium and sulfate were allowed to vary together keeping total sodium constant (see Figure IV-7).

In runs 404 and 420 with the improved reactor design (minimizing reactor oxidation), total system oxidation rates were 12.5% and 15.9% of the SO_2 absorbed respectively. In these runs, using sodium carbonate rather than sodium sulfate for makeup, the rate of sulfate precipitation and soluble sulfate losses in the cake approximated the rate of oxidation.

In runs 421 and 422 the high total dissolved levels significantly decreased the rate of sulfite oxidation in the scrubber system, but only slightly decreased oxidation in the reactor and dewatering systems. Although it is difficult to accurately determine the amount of oxidation in the reactor or dewatering systems independently, it is likely that oxidation in the reactor system decreased and that in the dewatering system remained constant or possibly increased. The high total dissolved solids level in the reactant liquor in runs 421 and 422 would reduce the rate of oxygen mass transfer to the reactant slurry. In the dewatering system, on the other hand, the dissolved solids level of the filtrate would be greatly diluted by washing of the cake, and oxygen mass transfer in the filter would not be expected to be appreciably different from that in runs at lower dissolved solids levels.

Although the high TDS decreased oxidation, the high active sodium levels also greatly reduced the amount of sulfate precipitation. Calcium sulfate levels in the filter cakes in both runs 421 and 422 were analyzed to be 4-5% of the total calcium-sulfur salts (molar basis). This amount of calcium sulfate precipitation along with about 2-2.5% sodium sulfate losses was sufficient to keep up with the sulfite oxidation estimated in run 421 (at 5% oxygen in the flue gas). However, it was not sufficient to keep up oxidation in run 422 (7.5% oxygen in the flue gas). This is confirmed in Figure IV-16, in which normalized active sodium concentration in the system liquors (active sodium/total sodium) is plotted with time. As shown, the ratio of active sodium to total sodium increases throughout run 421, but decreases throughout run 422.

The difficulty that may arise in operating with such high dissolved solids levels at oxidation rates in excess of 5% is that sodium sulfite is more soluble than sodium sulfate. Figure IV-17 shows the solubility limits of mixed sodium sulfite/sulfate solutions as a function of temperature. As oxidation rates climb, sulfate concentrations increase and sulfite levels correspondingly decrease. Thus, as oxidation increases, so does the saturation temperature and the probability of crystallizing sodium salts increases. For example, operating with a 5.0M total sodium concentration and with 5% oxidation, the equilibrium sulfate and sulfite concentrations in the regenerated liquor would be roughly 1.35M $SO_4^=$ and 1.15M $SO_3^=$ (according to Figure IV-7, taking into account redissolution of $CaSO_4$ in the thickener and assuming 2% solubles losses). As shown in Figure IV-17, the saturation temperature of this solution is about 24°C (75°F). If oxidation increases to 10%, then the sulfate will climb to about 1.85M and sulfite will drop to about 0.65M, and the saturation temperature will increase to 27-28°C (∿ 82°F).

The above discussion of saturation temperatures does not take into account the presence of chlorides in the solution, which can have a major impact on saturation tempuratures and the potential for crystallization of sodium salts. The concentration of chloride attained in the process liquor will primarily depend upon the level of chloride in the coal, the degree to which the cake is washed, and the total dissolved solids level in the liquor. For example, a high-sulfur coal containing 0.1 wt % chloride

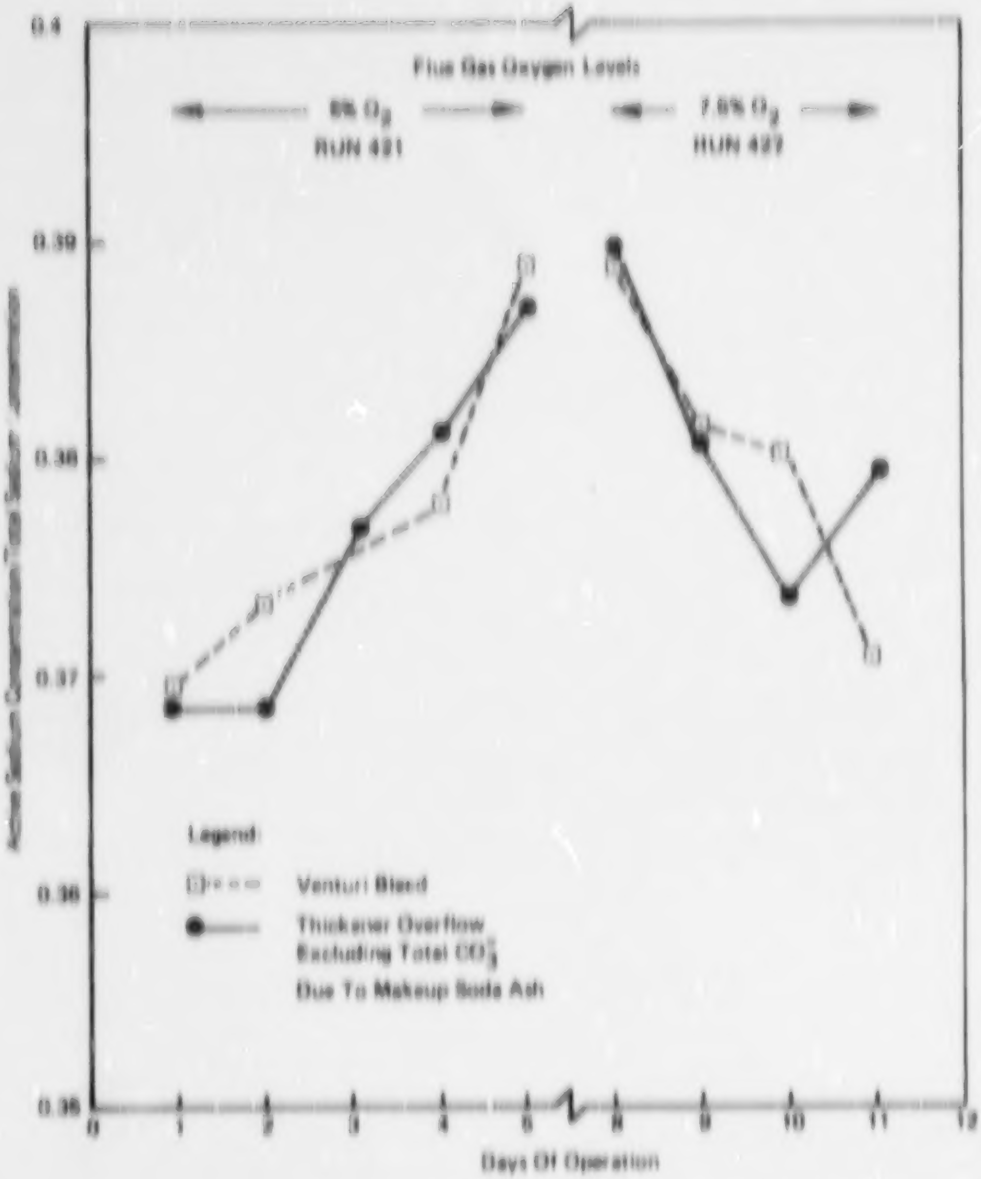


FIGURE IV-16 NORMALIZED ACTIVE SODIUM CONCENTRATION VS TIME IN RUNS 421 AND 422

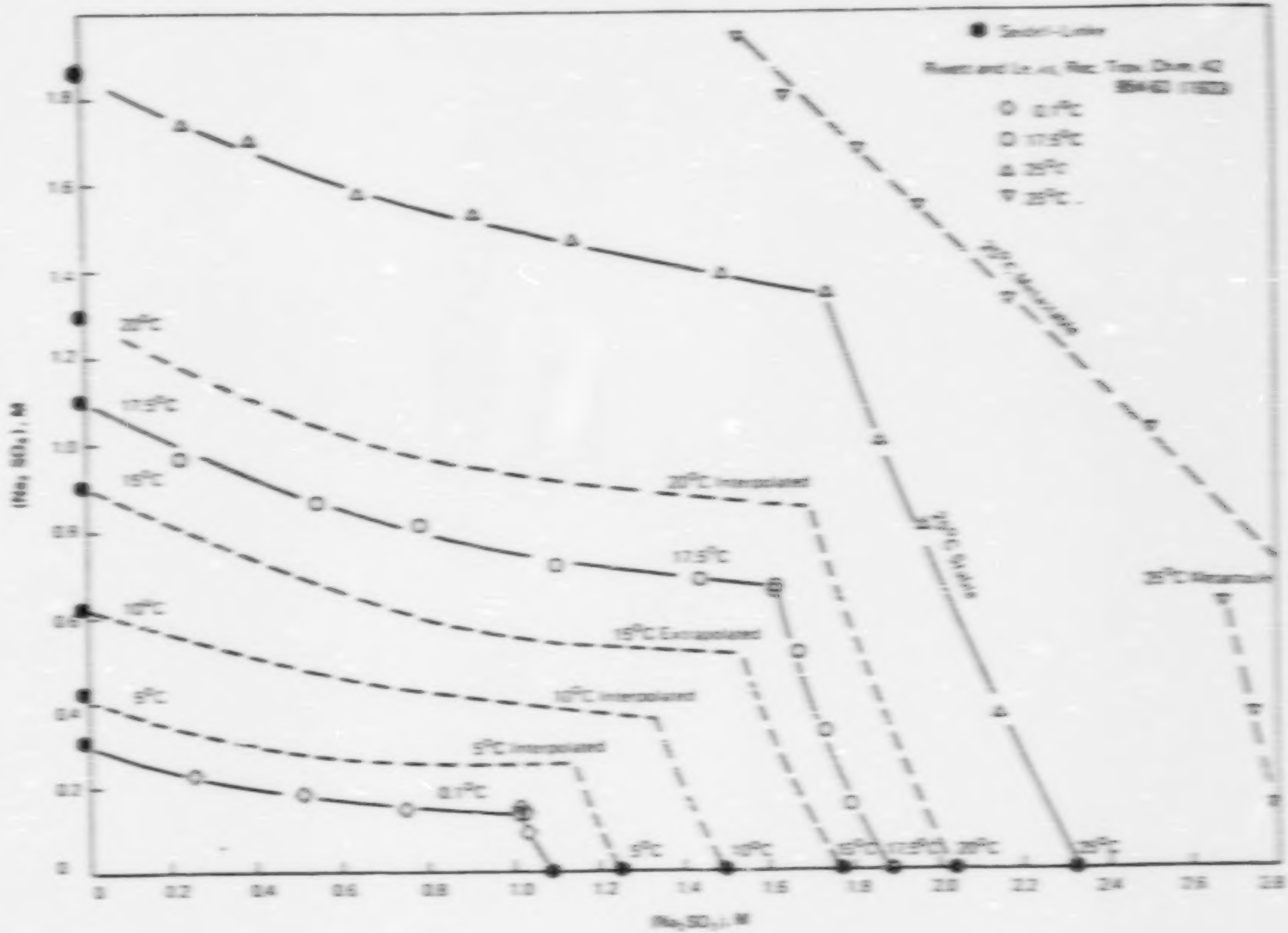


FIGURE IV-17 SOLUBILITIES OF Na_2SO_4 – Na_2SO_3 SOLUTIONS

will result in soluble chloride concentrations of 15,000 ppm to 30,000 ppm
(2.5 wt % to 5 wt % NaCl) in the liquor for a system operating with 12-15 wt %
TDS and the cake washed to 2.5% solubles. In a system operating at 35 wt %
TDS, on the other hand, chlorides levels of 35,000 ppm to 85,000 ppm would
be reached (5.5 wt % to 14 wt % NaCl) if the cake were washed to 2.5% solu-
bles. Thus, the effect of chloride can force operation at lower TDS levels
to prevent crystallization of sodium salts.

Solids Properties and Filter Operation

As discussed previously, solids properties are primarily a function of the
operating pH and the sulfate-to-active sodium ratio in the system liquor
as dictated by the total system oxidation. Increasing sulfate-to-active
sodium ratios in the system liquor results in decreasing solids content
of the filter cake and poorer cake washability. Solids properties also
tended to deteriorate with increasing reactor operating pH, particularly
using a CSTR for regeneration. This effect of pH was most pronounced at
higher sulfate-to-active sodium levels. In runs at high active sodium
concentrations (runs 421 and 422) in which sulfate-to-active sodium levels
were low (< 1.0), the CSTR produced reasonably good solids at operating
pH's up to 11.5. Similar solids were not generated in closed-loop runs
at lower active sodium levels (runs 401, 403, and 420) where sulfate-to-
active sodium levels were greater than 1.0.

The filter cake solids content was found to be an accurate measure in
general of the overall solids properties. High solids content was usu-
ally indicative of high filtration rates (lbs of dry solids/ft^2-hr),
minimal cracking on the filter and good wash efficiency, and acceptable
handling properties. In most cases, 45% insoluble solids was adequate
to ensure a cake with good washing characteristics, a reasonable filtra-
tion rate (> 25 lbs dry solids/ft^2-hr), and acceptable handling properties.
This means cakes that discharge readily, are relatively dry, and can be
handled and transported without excessive sticking to equipment.

Based upon these criteria the CSTR appears to be suitable for use where
oxidation rates do not exceed 12-15% of the SO_2 absorbed. The multistage
reactor, on the other hand, appears to be capable of producing good solids
at oxidation rates up to 20-25% of the SO_2 absorbed (see Figure IV-10).

These data were generated using a multifilament, polypropylene cloth with
a porosity equal to 30-50 cfm of air at a pressure drop of 1/2 inch H_2O.
In general, it was necessary to maintain the cake thickness below 1/2 inch
in order to minimize cracking and ensure good wash efficiency. This was
accomplished by adjusting drum speed (0.5 rpm to 1.0 rpm), drum submergence
(5% to 30%), and thickener underflow concentration. The exact conditions
depended upon the quality of the solids. In most cases with reasonably
good solids the thickener underflow was maintained between 15% and 25%
insoluble solids (even though higher slurry concentrations could frequently
be achieved) in order to ensure the proper cake thickness and provide a
pumpable slurry. Subsequent operation of the prototype system refined
these operating conditions and demonstrated that 5-10% higher solids

content could be achieved at equivalent process conditions. This can be attributed to a difference in filter cloth (monofilament versus multifilament) and better control of the thickener/filter operation.

One area of particular concern in the pilot plant operation was filter cloth blinding. In most cases blinding only occurred when poor solids were generated. However, in runs at high TDS levels the solids appeared to blind the cloth relatively easily, even though the cake solids content averaged almost 55% insoluble solids. Usually, the cloth did not require cleaning during a one-week run when solids content approached or exceeded 50% solids; however, during the high TDS runs (421 and 422) the cloth required cleaning once a day to ensure a reasonable rate of filter cake discharge. Although the reason for this is not known, it may have been due to crystallization of soluble salts in the cloth fibers.

Sodium Losses

Losses of soluble sodium in the pilot plant operation were primarily in the cake, with the amount of sodium lost a function of the cake quality, the wash ratio used and the TDS concentration in the liquor. At intermediate total dissolved solids levels (10-15%), two to three displacement washes were usually adequate with good cake quality to reduce solubles losses below 1%. In some early runs, though, optimal wash ratios were not used. Notably, in runs 401, 402, and 403, wash water was set at a low rate, even though more water was available. This resulted in a wash ratio of 1 in run 402 in which good quality solids were produced, and less than 1 in runs 401 and 403 in which poor cake was produced. At high total dissolved solids levels, wash ratios on the order of five or more displacement washes were required. Such wash ratios, as discussed previously, are unrealistically high for normal closed-loop operation.

While cake losses accounted for most of the sodium lost, there were also losses due to sampling, liquor entrainment in the outlet gas, and system leaks. In order to keep such losses at a minimum, all pump seal leakage and non-analytical samples (settling tests, clarity, and pH checks, etc.) were returned to the system. While in most runs at intermediate active sodium levels, such losses were maintained at or below about 1% of the SO_2 removed. In runs at high total dissolved solids levels, unaccounted for sodium losses are estimated to have run as high as 3% of the SO_2 absorbed. Although small, these losses do inflate the sodium makeup requirements for a small pilot operation and they also point up the greater care that must be taken at the higher concentrations to minimize and, to the extent possible, collect and return all system leaks.

One source of sodium loss that was evident in the high concentration runs was liquor entrainment in the scrubber off-gas stream. The amount of entrainment is not known, but there was sufficient buildup of salts on the exhaust fan to necessitate cleaning and rebalancing the fan each week.

System Operability and Reliability

Other than problems with poor solids properties and the buildup of salts on the fan during high-concentration runs, there were few operational problems. In general, the system was quite stable and handled upsets in inlet SO_2 and lime feed with ease.

In all but one run, no scale buildup of any kind occurred in the scrubber system. In run 403 where oxidation rates ran about 40% of the SO_2 removal, sulfite concentrations fell to 0.1M and below (approaching a dilute-mode operation), resulting in soluble calcium levels in excess of 500 ppm in the scrubber feed. In this run there was a small buildup of calcium sulfite and carbonate in the tray tower, causing an increase in the pressure drop across the tray tower from about 4 inches H_2O to 6 inches H_2O over the course of four days. In all other runs soluble calcium levels ranged from 15 ppm to 90 ppm and there was no evidence of scaling or solids deposition, even when mechanical problems in the dewatering system caused overflow of up to a few hundred ppm of suspended solids from the thickener.

One other problem of a process nature occurred in the runs at high TDS levels. During weekend shutdowns the high TDS levels resulted in precipitation of sodium salts from the liquor, despite insulation of tanks and flushing of all piping. The saturation temperature of the liquor in these runs was 20-25°C (68-77°F) compared with 8-15°C (45-60°F) for the lower concentration runs and on two occasions solution "froze" in the piping and at pipe/tank flanges. The pluggage was cleared by heating and water flushing. In large-scale systems this could be a more severe problem in high TDS operations, particularly where absorption of chlorides increases total dissolved solids levels.

D. CONCLUSIONS

In the concentrated mode using lime for regeneration, calcium sulfate will coprecipitate with calcium sulfite at sulfate precipitation rates equivalent to oxidation rates as high as 25% of the SO_2 removal. Solutions remain unsaturated with respect to calcium sulfate and have low soluble calcium concentrations. Process modes can be operated over a wide range of sodium solution concentrations achieving high SO_2 removal (greater than 90%) producing good quality filter cake (45% solids or greater) containing low soluble solids (2-5 wt % dry cake basis) with no sulfate purge required. The performance characteristics of concentrated lime regeneration modes are summarized in more detail below.

- SO_2 Removal -- SO_2 removal efficiencies in excess of 90% were easily achieved with the removal efficiency a function of sodium solution feed stoichiometry for any particular absorber design. In all closed-loop runs the feed stoichiometry (scrubber operating pH) was controlled to ensure better than 90% removal. For a given design, a slightly higher feed stoichiometry (or operating pH) was required for high sodium solution concentrations (30-35 wt % sodium salt solutions) than for moderate concentrations (10-15 wt %

sodium salt solution) to achieve the same removal efficiency because of the increase in SO_2 equilibrium partial pressure with the increase in sodium sulfite/bisulfite concentration.

- Lime Utilization -- Lime utilization in the range of 95-100% can be achieved with reactor holdup times of 25 minutes or greater when regenerating to a pH of 8 or higher. High utilizations can be achieved at shorter residence times if the regeneration reaction is not carried beyond neutralization of the bisulfite. Lime utilization decreases if regeneration is carried much beyond a pH of 12.5.

- Oxidation/Sulfate Control -- At active sodium concentrations above about 0.2M, calcium sulfate coprecipitates with calcium sulfite upon reaction of the sodium salt solution with lime. The sulfate/sulfite content of the precipitated calcium salts is related to the sulfate/sulfite concentrations in the reactor liquor by the following relationship:

$$\left(\frac{\text{mols } CaSO_4}{\text{mols } CaSO_3}\right)_{\substack{\text{reactor}\\ \text{solids}}} = 0.0365\left(\frac{[SO_4^=]}{[SO_3^=]}\right)_{\substack{\text{reactor}\\ \text{liquor}}} \qquad (1)$$

This relationship describes the coprecipitation phenomenon over the range of sulfite and sulfate liquor concentrations used in laboratory and pilot plant experiments ($[SO_3^=] > 0.2M$, $[SO_4^=]/[SO_3^=] = 0 - 6$). This method of sulfate precipitation is effective for oxidation rates up to about 25%. At any given active sodium concentration, high sulfate precipitation appears to be favored by either partial neutralization of the absorbent solution or regeneration to pH's well above neutrality (> 11.5), thereby reducing the sulfite concentration in the reactor liquor and maximizing the sulfate/sulfite ratio in the liquor.

In a properly designed concentrated dual alkali loop, the sulfate/sulfite ratio will self-adjust at steady-state so that the rate of sulfate precipitation equals the rate of sulfite oxidation. It is possible to achieve this balance over a wide range of active sodium and sulfate concentrations in dynamic response to changes in flue gas rates and oxygen and SO_2 concentrations.

For dual alkali systems operating with high TDS (in the range of 25-30 wt % sodium salt solutions) oxidation rates can be reduced by a factor of 2-3 from those encountered at lowered TDS levels (10-15 wt %). At such high TDS levels, the active sodium concentration as well as the sulfate concentration must be elevated in order to promote effective regeneration reactions and production of solids with acceptable dewatering properties. As a result, sulfate precipitation capability is limited.

- Solids Properties -- Single-stage CSTR and multistage reactor systems can produce solids,over a wide range of process conditions, which settle well and filter to insoluble solids contents of 45 wt % or higher. When using a CSTR as the regeneration reactor, solids properties deteriorate as the regeneration reaction is carried to a higher pH range with the degree of deterioration increasing from pH 7.5 to pH 12. This effect is worse for reactor holdup times of 60 minutes than for shorter reactor residence times (30 minutes). Using a CSTR, solids properties also decrease as the sulfate/sulfite ratio increases in the reactor liquor (at higher oxidation rates). In a single-stage CSTR, it is difficult to produce solids with acceptable properties (45 wt % insoluble solids) at process conditions consistent with sulfate precipitation and sulfite oxidation rates much beyond 15%.

  Good quality solids can be produced over a wider range of pH and sulfate concentration using a two-stage reactor system, consisting of a short residence time reactor (5-10 minutes) followed in series by a longer residence time second stage (20-40 minutes). This multistage system produces good solids at pH levels up to about 12.5 and at sulfate/sulfite ratios required for sulfate precipitation rates equivalent to about 25% oxidation.

- Sodium Losses -- For a filter cake containing 50% insoluble solids, the soluble solids content of the cake can be reduced to 2-3% (dry cake basis) using the amount of filter cake wash water which would normally be available when operating closed-loop in a high-sulfur coal boiler application. At TDS levels in the range of 10-15 wt %, two to three displacement washes are effective in reducing the soluble content of the cake to 2-3 wt %. Of this material, 0.5-1 wt % soluble sodium salts appears to be occluded in the calcium salt crystals and cannot be washed regardless of the amount of wash water used. About two to three displacement washes are available for high-sulfur coal applications. At high TDS concentrations (30%), four to five displacement washes are necessary to reduce solubles to the 2-3% level. With only three displacement washes, solubles losses at high TDS concentrations can be expected to be roughly twice those when operating at 10-15 wt % TDS levels in the absorbent solution.

  At the lower TDS levels, sodium makeup requirements are on the order of 2-3% of the total alkali requirement (mol basis). That is, roughly 2-3% of the sulfur absorbed from the flue gas leaves the system as sodium salts with the remainder as calcium salts.

  From the above considerations, operating a concentrated lime mode with TDS in the range of 10-15%, the single-stage CSTR can produce good quality solids (65 wt % or greater) containing 2-3 wt % solubles at system oxidation rates up to 15%. When using the multistage reactor system the operability of the process is extended to oxidation levels in the range of about 25%. Increasing TDS reduces oxidation but requires more wash water to produce the same cake solubles content. At two to three displacement washes, the solubles content of the cake is proportional to the TDS levels in the system loop.

- System Reliability/Operability -- In concentrated modes using lime for regeneration, soluble calcium concentrations range from 15-90 ppm with the calcium concentration generally decreasing with increasing sulfite concentration. No scaling or deposition of solids was observed in the scrubber loop during any of the concentrated mode operations. Scrubber operation and SO_2 removal were easy to control. The regeneration reaction is stable and easy to control, but should be kept at a pH below about 8 if operating with a single-stage regeneration reactor. Increasing the TDS level in the system raises the sodium salt saturation temperature, increasing the potential for solid sodium salt crystallization in elements of the system which are permitted to cool.

V. SULFURIC ACID TREATMENT -- CONCENTRATED MODE

A. LABORATORY RESULTS

1. Introduction

The inherent sulfate precipitation which was observed during lime regeneration of concentrated sodium sulfite/bisulfite/sulfate solutions shows promise of being able to control sodium sulfate at manageable levels when system oxidation rates are in the range of 25-30%. An alternate method, capable of dealing with significantly higher oxidation rates, involves the acidification of the process liquor with sulfuric acid in the presence of solid calcium sulfite to precipitate dissolved sulfate as gypsum. The overall reaction involved in this treatment process is:

$$Na_2SO_4 + H_2SO_4 + 2CaSO_3 \cdot 1/2H_2O(s) + 3H_2O \rightarrow 2CaSO_4 \cdot 2H_2O(s) + 2NaHSO_3 \quad (2)$$

thus, although additional sulfate is introduced as sulfuric acid, both that sulfate and the Na_2SO_4 should be precipitated as gypsum. On the basis of the 1:1 relationship between sulfate (sodium) to be precipitated and sulfuric acid required, a reaction efficiency (theoretically 100% based on equation 19) can be defined by expressing the moles of Na_2SO_4 removed from the process stream as a percentage of the moles of H_2SO_4 added:

$$\text{Efficiency} = \left(\frac{\text{mole } Na_2SO_4 \text{ removed}}{\text{mole } H_2SO_4 \text{ fed}}\right) \times 100\%$$

The primary acid consuming reaction is the dissolution of $CaSO_3 \cdot 1/2H_2O$ by converting it to the soluble calcium bisulfite:

$$2CaSO_3 \cdot 1/2H_2O + H_2SO_4 + H_2O \rightarrow CaSO_4 \cdot 2H_2O(s) + 2HSO_3^- + Ca^{++} \quad (16)$$

The dissolved calcium ion produced in this reaction can then react with the sodium sulfate to be precipitated to form gypsum:

$$Ca^{++} + SO_4^= + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O(s) \quad (17)$$

In addition to the primary reaction discussed above, other equilibria would likely be involved and would result in reaction efficiencies of less than 100%. At the acidic conditions required to dissolve calcium sulfite (pH = 2-3), measurable amounts of sulfurous acid and possibly bisulfate ion could exist in solution due to the acid equilibrium reactions:

$$HSO_3^- + H^+ \rightleftarrows H_2SO_3 \quad (18)$$

$$SO_4^= + H^+ \rightleftarrows HSO_4^- \quad (19)$$

In practice, the streams to the acid treatment could contain other sulfites, carbonates and possibly hydroxide. In such cases, sulfuric acid consumption would be increased and reaction efficiency reduced.

The most acidic process stream normally available from which sulfate could be precipitated -- scrubber effluent -- normally contains on the order of 0.05M Na_2SO_3. Even well washed filter cake could contain calcium carbonate or unreacted lime. Depending upon washing efficiency, significant amounts of Na_2SO_3 and NaOH could also be present. If the calcium sulfite were obtained as a thickened slurry from the regeneration section -- attractive because of the ease of obtaining it and transferring it to the acidification process -- significantly larger amounts of NaOH and Na_2SO_3 would be present. The NaOH and Na_2SO_3 will react with H_2SO_4 according to the reactions:

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O \qquad (20)$$

$$2Na_2SO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2NaHSO_3 \qquad (21)$$

consuming H_2SO_4 and producing additional soluble sulfate in solution. Any lime or limestone present in the calcium sulfite feed will react with sulfuric acid:

$$Ca(OH)_2(s) + H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O(s) \qquad (22)$$

$$CaCO_3(s) + 2H_2SO_4 \rightarrow H_2O + CaSO_4 \cdot 2H_2O(s) + CO_2\uparrow \qquad (23)$$

These reactions will consume additional acid but will not add additional sulfate to the solution because of the accompanying precipitation of gypsum.

As a point of departure for the subsequent laboratory studies, a very approximate estimate was made of the pH to which the solution would need to be taken for the regeneration reaction to proceed, based upon very dilute solution solubility product and acid dissociation constants. For the precipitation of gypsum to occur, its apparent solubility product in water:

$$K_{sp}' = [Ca^{++}] [SO_4^{=}] = 2 \times 10^{-4} \qquad (24)$$

would need to be exceeded. If $[SO_4^{=}]$ were 1.0M initially, $[Ca^{++}]$ would need to exceed $2 \times 10_4$ M for precipitation to occur. For the precipitation of gypsum to continue until $[SO_4^{=}] = 0.1M$, the calcium ion concentration in solution would need to rise further to about $2 \times 10^{-}_{3}M$.

To achieve calcium levels of this magnitude in the presence of the very insoluble calcium sulfite, $[SO_3^{=}]$ would need to be held to a very low level by converting it to bisulfite ion. Considering the apparent solubility product of calcium sulfite:

$$K_{sp}' = [Ca^{++}] [SO_3^{=}] = 10^{-7} \qquad (25)$$

a calcium ion concentration of about 10^{-3} would require that the level of sulfite ion be held to about $10^{-4}M$. Now, to achieve that sulfite ion level in a solution containing sulfite/bisulfite at about 0.5%, the second ionization constant of sulfurous acid:

$$K = \frac{[SO_3^{=}]\,[H^+]}{[HSO_3^-]} = 10^{-7} \qquad (26)$$

would indicate that $[H^+] > 5 \times 10^{-3}$, or a pH in the vicinity of 3, would be required.

2. Experimental Results and Discussion

Prior to studying the acidification reaction in the laboratory in a continuous reactor, a number of batch experiments (in which H_2SO_4 was added to Na_2SO_4/$CaSO_3$ slurries) were conducted in a sealed reactor to better define the operating pH range and, more importantly, to establish the SO_2 partial pressure levels generated within the reactor. The Na_2SO_4/$CaSO_3$ slurries were charged into the reactor, and the headspace above the liquid was purged briefly with SO_2 to eliminate air before sealing the reactor. Sulfuric acid was then introduced into the sealed system from a pressure-equalized addition funnel while monitoring the pressure within the reactor.

The batch experiments indicated that the operating pH would, in fact, be in the range of 2.5-3.0. Throughout the course of sulfuric acid addition, the pressure within the reactor indicated that the partial pressure of SO_2 was less than 1 atmosphere, and a sealed reactor capable of withstanding a positive internal pressure would not be required for the reaction. The reactor could be operated at ambient pressure vented to the atmosphere as long as the reactor vent tube was of a sufficiently narrow bore to minimize mixing between the internal headspace gas and the outside air.

On the basis of the background information obtained from batch experiments, the effects of a number of experimental variables on the regeneration reaction were studied in the laboratory using the CSTR described in Chapter III, Section A. Since it was the only material available in quantity at that time, the calcium sulfite used in these studies was unwashed calcium sulfite filter cake produced in an earlier ADL pilot plant run in which concentrated sodium bisulfite/sulfite/sulfate solutions were regenerated with lime. This material contained relatively large amounts of calcium carbonate and calcium sulfate along with lesser amounts of sodium salts as the following composition indicates:

Compound	Mol Percent
$CaSO_3$	69.2
$CaCO_3$	15.4
$CaSO_4$	10.5
Na_2SO_4	[illegible]

Compound	Mol Percent
NaOH	1.0
Na_2SO_3	0.5

This composition is based upon chemical analyses and material balances for the pilot plant runs in which the material was produced. This filter cake was slurried with a simulated acidic scrubber effluent solution containing, in all cases, Na_2SO_3, 0.05M; $NaHSO_3$, 0.40M; and Na_2SO_4 at either 0.75M or 0.37M. This slurry comprised one stream to the CSTR and either 4.5M or 9.0M H_2SO_4 was fed as the other reactant.

Both phases of the reactor effluent slurry were analyzed in detail. In the liquid phase, in addition to measuring total soluble calcium ion and sulfate ion, measurements of total oxidizable sulfur (TOS) and total acidity $(H^+)_{tot}$ were made by titration. The TOS concentration is the total concentration of all sulfur (IV) species present, and the total acidity $(H^+)_{tot}$ is the sum of all acidic protons (titratable to pH = 9) in the solution. These relationships may be expressed as follows:

$$[TOS] = [H_2SO_3] + [HSO_3^-] + [SO_3^=]$$

$$[H^+]_{tot} = [HSO_3^-] + 2[H_2SO_3] + [HSO_4^-] + [H^+]$$

By subtraction, the "excess acidity", $([H^+]_{tot} - [TOS])$ equals

$$[H^+]_{tot} - [TOS] = [H_2SO_3] + [HSO_4^-] + [H^+] - [SO_3^=]$$

However, under the range of conditions over which the reaction was studied (see Table V-1), H_2SO_3 and HSO_3^- are the predominant species present. At pH ≤3, $[SO_3^=]$ is virtually zero and $[H^+]$ is less than 0.01M.

The dilute solution value for the second ionization of sulfuric acid, pK_2, is about 2; however, dissociation of HSO_4^- increases as ionic strength is increased. In the CSTR experiments performed, the ionic strength was in two general regions -- 2.25 (experiments 6-7) and 1.4 (experiments 9-10). Marshall and Jones[8] report values of pK_2 for H_2SO_4 of 0.82 and 1.1, respectively, at those ionic strengths. At the conditions studied here, then, HSO_4^- exists only in small concentrations -- the concentration of HSO_4^- is at most 2% of the H_2SO_3 concentration in the solution. The two measurements H^+_{tot} and TOS, allow one to determine the amounts of H_2SO_3 and HSO_3^- present in the reaction effluent.

The results obtained from the CSTR studies are shown in Table V-1. In the three experiments in series 6, the regeneration of 0.75M Na_2SO_4 solution was studied as a function of pH ranging from about 2.35 to 3.15 with reactor residence time and temperature held constant. In series 7, temperature and residence time were varied. In the final three experiments, 0.37M Na_2SO_4 was studied as a function of pH.

TABLE V-1

[illegible]

Expt.^{a,b}	[illegible]	Residence Time (min)	Temp (°C)	pH	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Effective [illegible]^{c}	Observed^{d}	Corrected^{e}
9-a	0.75	30	33	3.1	1.36	1.51	0.25	0.026	8.5	0.090	0.49	0.30	0.70
9-b	0.75	30	34	2.9	1.47	1.60	0.29	0.028	7.5	0.25	0.57	0.30	0.66
9-c	0.75	30	34	2.3	1.46	1.58	0.26	0.026	5.0	0.30	0.48	0.75	0.37
7-a	0.75	15	34	<2.0	1.52	1.60	0.27	0.036	9.2	0.21	0.61	0.42	0.78
7-b	0.75	30	34	2.6	1.59	1.75	0.25	0.030	7.5	0.22	0.60	0.46	0.63
7-c	0.75	15	32	2.8	1.56	1.72	0.25	0.032	8.2	0.21	0.62	0.37	0.57
8	0.37	15	33	2.8	1.23	1.29	0.14	0.062	5.8	0.26	0.69	0.33	0.47
10-a	0.37	15	33	2.7	1.42	1.48	0.075	0.069	5.1	0.26	0.80	0.29	0.35
10-b	0.37	15	33	2.2	1.36	1.86	0.055	0.107	5.9	0.22	0.85	0.22	0.25

---

[a] Solution to be regenerated: simulated scrubber effluent:

[illegible] = 2.4 M
[illegible] = 0.25 M
[illegible] = as indicated
pH = 5.4 – 5.5

[b] [illegible] feed maintained at 110 – 120% of stoichiometric except:

Expt. 9-c was deficient; [illegible] in effluent
Expt. 10-a, 10-b fed at 200% of stoichiometric

[c] Mol fraction of entering [illegible] actually removed.

[d] [illegible] – mols soluble [illegible] [illegible] charged.

[e] Observed efficiency corrected for effect of alkaline impurities in [illegible] feed.

The effect on the regeneration reaction of reducing the pH from 3.15 to 2.9 was an increased TOS concentration as additional calcium sulfite dissolved at the lower pH. In turn, the concentration of $SO_4^=$ decreased as the soluble calcium which was produced reacted with SO_4 to precipitate gypsum. As indicated by the lower $SO_4^=$, the "effective Na_2SO_4 removal" from the simulated scrubber stream ($\Delta Na_2SO_4/Na_2SO_4$) was higher at the lower pH (this ratio is corrected for all sulfate removed which entered as H_2SO_4 or in the calcium sulfite filter cake).

As the pH was decreased to 2.9, the concentration of TOS increased by 0.1M but the total acidity increased by 0.17M as a result of the higher concentration of H_2SO_3 present at the lower pH. The ratio of H_2SO_3/HSO_3^- had risen from 0.09 to 0.15 as shown in the table. The formation of H_2SO_3 consumed H_2SO_4 and should have reduced the efficiency of H_2SO_4 utilization. Thus the increased effective sulfate removal at pH 2.9 was compensated for by the decrease in efficiency of H_2SO_4 utilization to produce an essentially constant overall "observed efficiency" of H_2SO_4 utilization = ΔNa_2SO_4/total H_2SO_4 fed.

Since the calcium sulfite cake which was used contained a large amount of $CaCO_3$ as well as other impurities which would consume H_2SO_4, the effects of the non-calcium sulfite species were taken into account and a "corrected efficiency", which should have been realized if pure calcium sulfite had been fed, was computed. As shown in the table, H_2SO_4 utilization efficiency would have been in the range of 0.6 to 0.7.

In experiment 6-c, the pH was further lowered to 2.35; but, upon analysis of the reaction products, it was found that no solid calcium sulfite remained in the effluent slurry. The results of this experiment show the important consequence of operating "calcium sulfite limited" (less than the stoichiometric amount of calcium sulfite); both the effective Na_2SO_4 regeneration and H_2SO_4 utilization dropped significantly. In experiments 6-a and 6-b, about 20% and 10%, respectively, of the calcium sulfite fed remained in the reaction solids.

Decreasing the reactor residence time to 15 minutes and raising the reaction temperature from 34 to 51°C (series 7) did not produce significant changes in effective sulfate regeneration or reaction efficiency.

When the concentration of Na_2SO_4 was reduced to 0.37M in experiment 9, an effective Na_2SO_4 removal of 0.66 was observed at pH = 2.4, a value slightly higher than in the corresponding experiment at the higher sulfate concentration (7-a); however, both the observed and corrected H_2SO_4 utilizations were significantly lower. (About 5% of the calcium sulfite fed remained in the effluent solids.) An important factor in the decreased H_2SO_4 utilization is the fact that as the incoming concentration of Na_2SO_4 is decreased while the concentration of Na_2SO_3 in the solution is held constant, proportionately more of the acid is utilized for the acidification of Na_2SO_3 than for the regeneration of Na_2SO_4. Lowering the pH to 2.2 produced an even larger effective Na_2SO_4 removal but sulfuric acid utilization efficiency decreased even further.

Thus, as is not unexpected, removing a given amount of Na_2SO_4 per pass through the reactor will result in increasingly poorer utilization of sulfuric acid as the Na_2SO_4 level in the incoming stream decreases. As a consequence, for a fixed process oxidation rate, the Na_2SO_4 regeneration process will be increasingly inefficient as the required steady state Na_2SO_4 level in the process is lowered.

B. PILOT PLANT RESULTS

The evaluation of the sulfuric acid slipstream treatment process involved both open-loop reactor tests to confirm and extend the laboratory performance data, and the use of the sulfuric acid treatment system in conjunction with the complete dual alkali absorption/regeneration loop operating in a concentrated lime mode. In both sets of the tests, the sulfuric acid reactor system was operated in a similar manner. Filter cake slurry was fed continuously to the reactor together with 20-30 wt % sulfuric acid at a rate sufficient to maintain a prescribed reactor pH in the range of 2.3 to 3.3.

The filter cake slurry was made up as required on a batch basis. In the integrated system operation, a portion of the filter cake generated during the run was slurried with venturi recycle liquor. In the open-loop tests, the slurry was prepared using filter cake saved from prior dual alkali operations and either simulated venturi effluent liquor or simulated thickener underflow liquor.

The sulfuric acid reactor consisted of a baffled 30-gallon Pfaudler kettle vented to the atmosphere. The level in the reactor was adjusted to maintain approximately a 30 minute reactor holdup time. Effluent from the reactor was sent to a 6-inch solid bowl centrifuge for the separation of the solids. In the full system operation, the centrate was returned to the lime regeneration reactor.

A schematic of the overall system operation is provided in Figure V-1.

1. Sulfuric Acid Reactor Performance

The results of the sulfuric acid reactor pilot plant tests confirmed the basic laboratory findings. The reaction proceeds readily to completion with formation of a gypsum product with good settling properties. Preliminary pilot tests showed that a 30 minute reactor holdup time is sufficient for essentially complete conversion; and the optimum pH appeared to be above 2.35.

Subsequent runs were then made over a range of pH from 2.6 to 3.3 in three different operating regimes: Na_2SO_4 limited, $CaSO_3$ limited, and approximately stoichiometrics ratios of Na_2SO_4 to $CaSO_3$. The results of these runs are summarized in Table V-2 and Figure V-2.

As would be anticipated, the runs with $Na_2SO_4/CaSO_3$ feed ratios nearest to the theoretical stoichiometric requirement of 0.5, resulted in the

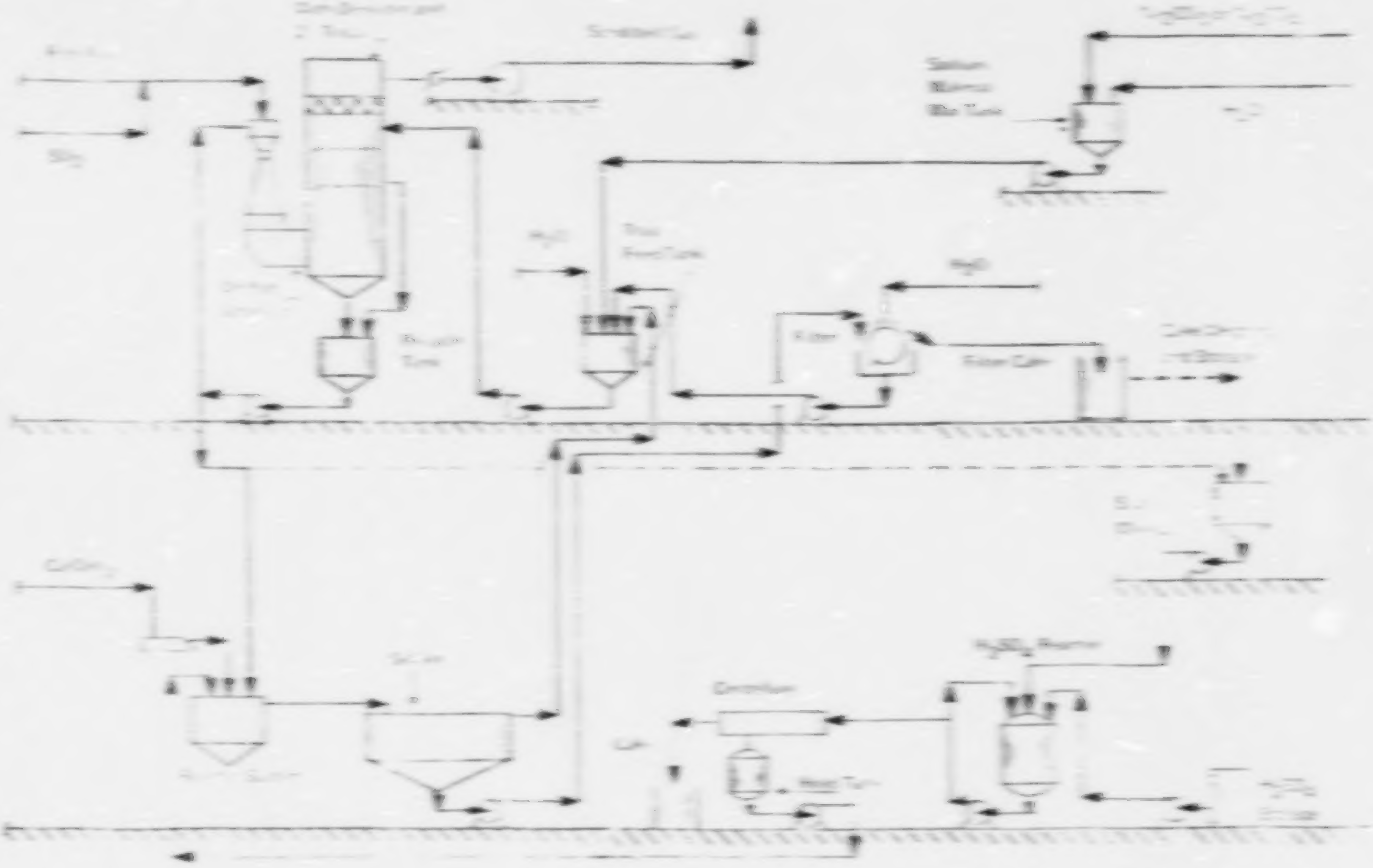

Scrubbed Gas
H2O
H2O
Filter
Filter Cake
Centrifuge
H2SO4 Reactor

Figure V-3 Schematic Flow Diagram of Pilot Plant Operation For Sulfuric Acid Treatment [illegible]

TABLE V-2

SUMMARY OF SULFURIC ACID SLIPSTREAM TREATMENT RESULTS - PILOT PLANT

Sulfuric acid Reactor Conditions: τ = 30 min (CSTR) Residence Time
T = 80 - 110°F
pH = 2.6 - 3.3

Feed Streams: Solids Source - Washed Filter Cake
Liquor - Scrubber Bleed or Thickener Underflow
Acid Strength = 2.5 - 3.0 M H_2SO_4

Operating Regime	Run No.	Feed Composition Wt % Solids	Liquid Composition $[SO_3^=]$, M	pH	Solids Composition, (wt%) $CaSO_3$	$CaSO_4$	mole Na_2SO_4 / mol $CaSO_3$	Reactor Efficiency[a] Observed	Corrected[b]
Na_2SO_4 Limited	056	24.	0.63	11.5	74	10	0.32	0.22	0.33
	055	18.5	0.39	6.9	82	7	0.38	0.37	0.45
Stoichiometric	016-2	19.5	0.74	6.9	79	17	0.46	0.52	0.55
	016-1	19.	0.76	7.1	80	15	0.48	0.56	0.59
	016-3	14.5	0.83	6.9	76	18	0.54	0.66	0.68
	017-2	18.5	0.80	7.2	78	19	0.57	0.61	0.70
$CaSO_3$ Limited	050	13.	0.58	6.9	78	11	0.60	0.43	0.52
	017-1	18.5	0.90	7.1	78	19	0.67	0.39	0.44
	052	10.5	0.54	11.0	74	13	0.75	0.22	0.27
	051	11.	0.57	7.0	74	11	0.76	0.28	0.32
	053	26.5	1.07	11.5	36	52	0.95	0.10	0.13

[a] $\frac{\text{mole } Na_2SO_4 \text{ in} - \text{mole total } SO_3^= \text{ out}}{H_2SO_4}$ = Efficiency

[b] Efficiency corrected for NaOH, $CaCO_3$ and Na_2SO_3 alkalinity in feed slurry

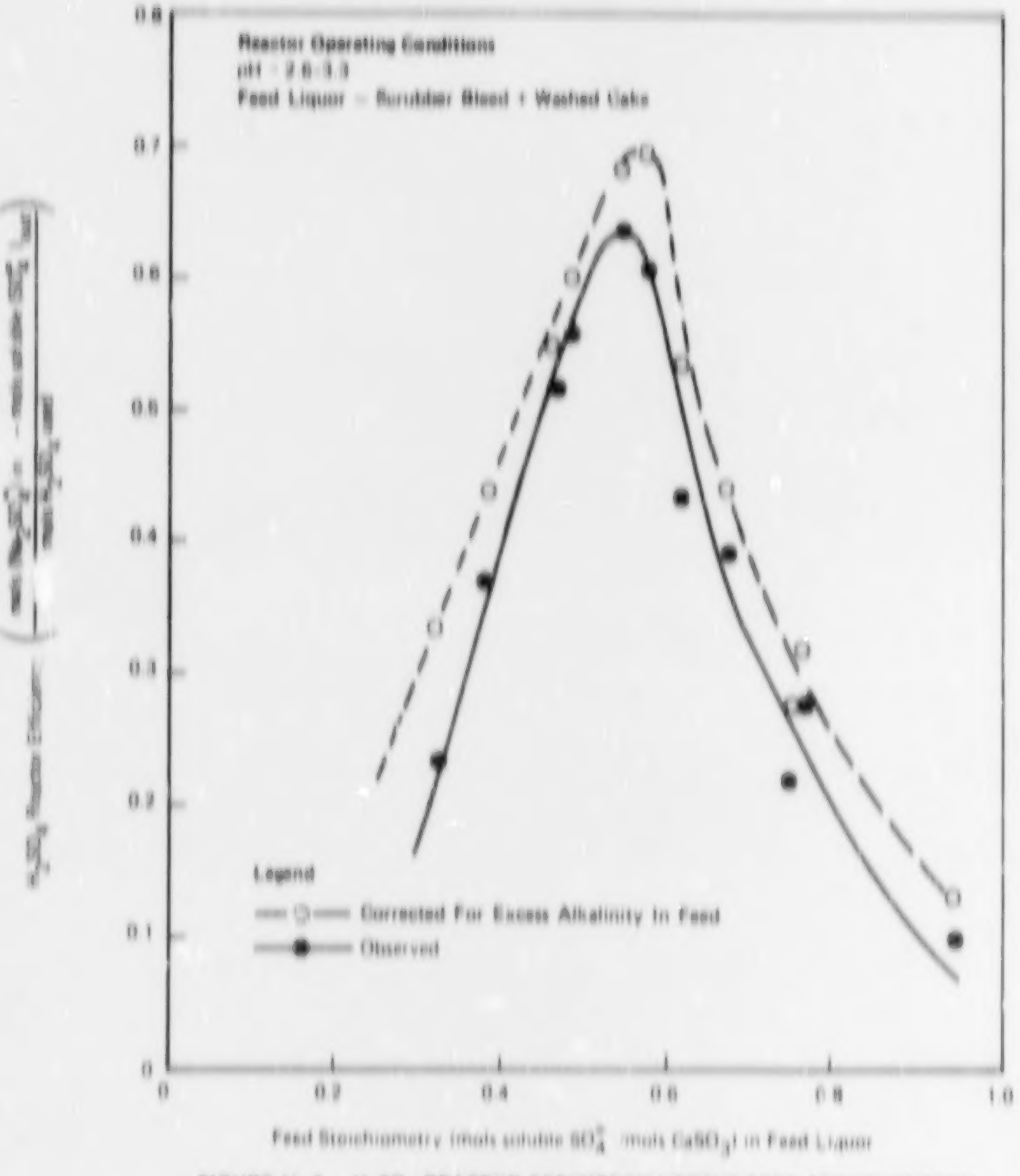


FIGURE V-2 H_2SO_4 REACTOR EFFICIENCY VERSUS FEED STOICHIOMETRY

highest reactor efficiencies. (Here, efficiency is defined as the decrease in mols of sodium sulfate divided by the mols of sulfuric acid used -- (mols Na_2SO_4 in-mols total $SO_4^=$ out)/mol H_2SO_4 used.) The highest efficiency attained in the pilot plant operations was 0.64 at a ($Na_2SO_4/CaSO_3$) feed ratio of 0.54. In cases where the feed ratio was greatly different from stoichiometric, the reactor efficiencies were found to decrease markedly. In the sulfate limited regime, acid is wasted dissolving $CaSO_3$ which is not used; and in the $CaSO_3$ limited regime, acid is wasted neutralizing and adjusting the pH of extra feed solution.

The pilot plant data plotted in Figure V-2 cover a range of operating conditions including sulfate and sulfite concentration, reactor pH, ionic strength, and alkalinity content of the feed slurry. The chemistry of the system indicates that all of these factors will influence the efficiency of the reaction. Since all of these effects are confounded to some degree in the pilot plant results, the correlation of reactor efficiency with feed stoichiometry contains secondary factors other than analytical error that contribute to the data scatter. The efficiency/feed stoichiometry curve given in Figure V-2 should be considered a generalized representation.

An attempt was made to extract the effects of feed alkalinity in order to clarify the observed performance. This involved adjusting the sulfuric acid used in each run to account for that acid used in neutralizing $CaCO_3$, NaOH and Na_2SO_3 in the feed. The "corrected" reactor efficiencies based upon these adjusted acid requirements are listed in Table V-2 and are superimposed in Figure V-2. As would be expected, the magnitude of the correction was generally greatest for the runs using simulated thickener underflow and for runs in the $CaSO_3$ limited regime where excess solution was fed.

The effects of sulfate concentration and reactor pH were specifically addressed in the laboratory program. This work showed that the optimum reactor operating pH is roughly 2.5 to 3.0, the range in which almost all pilot plant runs were made. Furthermore, as sulfate concentrations increase in the reactor feed slurry, reactor efficiency improves. This effect is not clearly demonstrated in the pilot plant data due to the great range of feed stoichiometry, which has a more pronounced influence on reactor performance.

Finally, the ionic strength of the reactor effluent slurry has a small effect on efficiency since it determines, along with temperature, the solubility product of gypsum. As ionic strength increases, the solubility product should also increase and, therefore, reactor efficiency should correspondingly decrease. Although the effect on reactor efficiency is too small to be observed, the increase in the gypsum solubility product with ionic strength was observed. Figure V-3 shows the apparent solubility product curve for gypsum (calculated by molar concentrations) predicted by ADL along with solubility data generated in both the pilot plant and laboratory tests. For all but a few runs, the experimentally determined

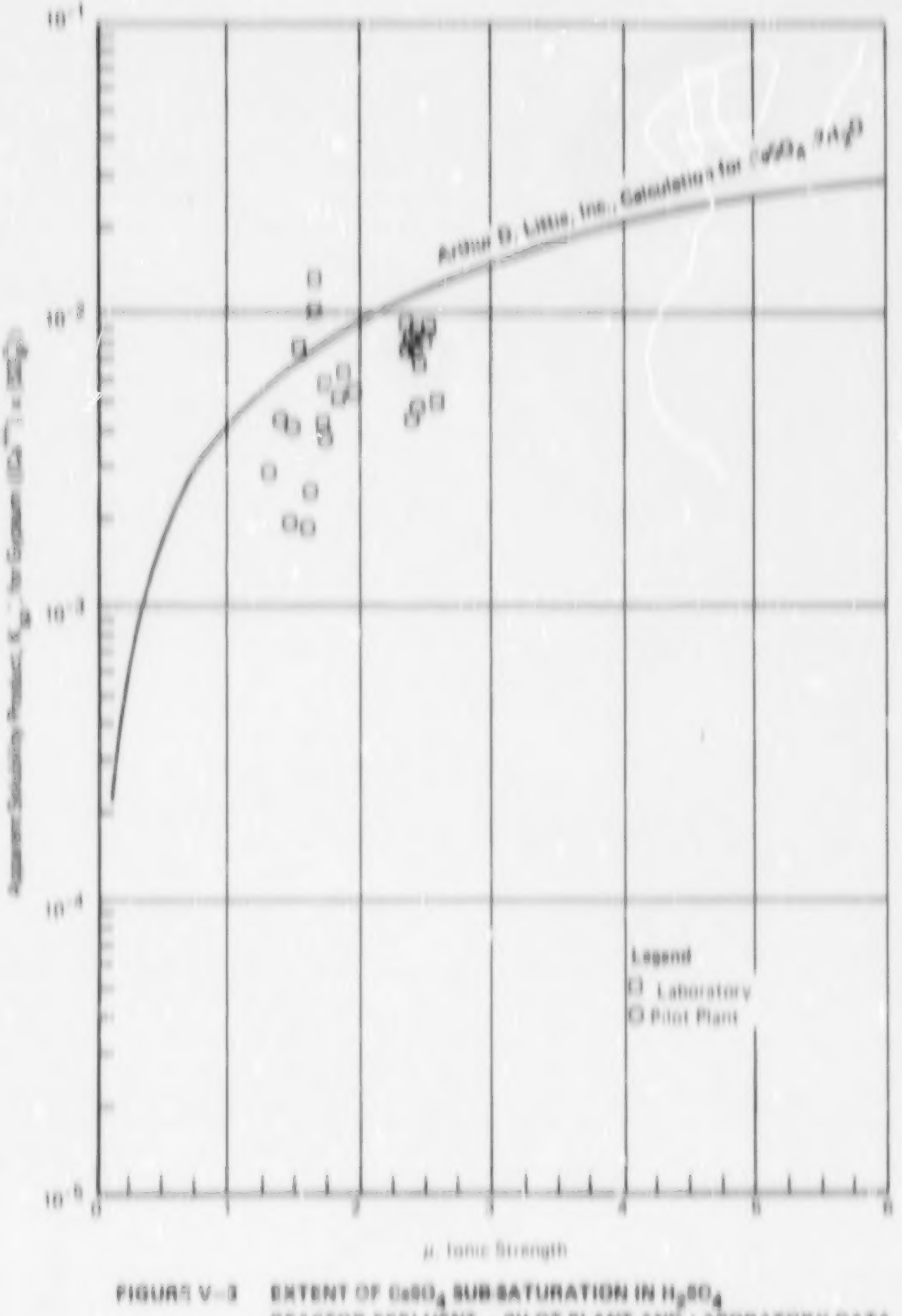


FIGURE V-3 EXTENT OF $CaSO_4$ SUBSATURATION IN H_2SO_4 REACTOR EFFLUENT – PILOT PLANT AND LABORATORY DATA

values of the apparent solubility product fall slightly below the predicted curve (predicted by the method of Rusch and Meissner), indicating that the solutions may not have been saturated with respect to $CaSO_4 \cdot 2H_2O$. The validity of this predicted solubility product curve is demonstrated by the gypsum saturated data presented in Chapter VII.

The pilot plant solubility data shown in Figure V-3 correspond to soluble sulfate concentrations of 0.1M to 0.4M $SO_4^=$ and calcium levels of 0.01M to 0.04M Ca^{++} (400 ppm to 1,600 ppm). The lowest effluent sulfate levels, and therefore highest calcium levels, were achieved in cases where the reactor efficiency was highest.

Although the highest efficiency achieved in the pilot plant tests was 0.64, it is reasonable to assume that refinements in the operating conditions and slight adjustments in the process configuration could raise efficiencies to above 0.7. For example, the reactor vent gas could be recovered and used for pre-acidifying the incoming filter cake slurry. Also, if Na_2SO_4 is used for the makeup sodium value, then this could be added either as a concentrate or solid directly to the sulfuric acid reactor feed slurry.

2. Integrated System Operation

Two closed-loop pilot plant tests were run for extended periods with the sulfuric acid reactor system operating on a slipstream from the dual alkali process. The overall system was operated in the concentrated active sodium mode using hydrated lime for absorbent regeneration. The first test, run 016, was made at an inlet SO_2 level of 2,250 ppm. The second test, run 017, was conducted at an inlet SO_2 level of 650 ppm. The process conditions and overall results are summarized in Table V-3.

In both runs the operation of the sulfuric acid treatment system was similar to the open-loop tests as previously described. Washed filter cake generated during the run was used as the $CaSO_3$ source and venturi recycle liquor provided Na_2SO_4. The dual alkali process liquor was originally primed to a soluble sulfate level of about 0.8M to ensure that sufficient sulfate was present to produce high reactor efficiency. The rates of feed of cake slurry and sulfuric acid were initially set such that the total anticipated oxidation in the dual alkali system could be sustained by the combined sulfate precipitation in the absorbent regeneration reactor and sulfuric acid reactor and by the loss of soluble sulfate in the waste cake.

The performance of the sulfuric acid system in these runs has been discussed in connection with the sulfuric acid reactor performance in the previous section. Overall, the results were very good. Efficiencies ranged from 0.38 to 0.64 throughout both tests, and the average efficiency over each test was greater than 0.5. The gypsum produced had good dewatering properties. Centrifuge cake containing up to 70 wt % insoluble solids could be obtained by close control of the centrifuge feed rate.

TABLE V-3

SUMMARY OF CLOSED-LOOP PILOT PLANT RUNS

Sulfuric Acid Treatment Mode

Run No.	016	017
Dual Alkali Process Operation		
Inlet SO_2 Level, ppm	2,250	650
SO_2 Removed, ppm	2,050	530
Scrubber Bleed: pH	6.1	6.1
[TOS], M	0.35	0.5
$[SO_4^=]$, M	0.7	0.8
Overall System Oxidation		
Equivalent ppm SO_2 (avg.)	570	400
% ΔSO_2 (avg.)	28%	70%
Sulfate Precipitation in Lime Reactor:		
Equivalent ppm SO_2 (avg.)	250	100
% ΔSO_2 (avg.)	12%	18%
Calcium Feed:		
mols $Ca(OH)_2$/mol ΔSO_2	1.33	1.83
mols $Ca(OH)_2$/mol sulfur input	1.06	1.01
H_2SO_4 Treatment System Operation		
H_2SO_4 Feed, (mols H_2SO_4/mol ΔSO_2)	0.28	0.63
Reactor Efficiency	0.52-0.64	0.38-0.61
Sulfate Precipitation:		
Equivalent ppm SO_2	280	180-300
% of ΔSO_2	14%	34-57%
Centrifuge Cake Composition:		
Insoluble Solids (% total wt)	60-70	53
Soluble Solids (% dry cake)	6-7	15

The primary effect of the sulfuric acid slipstream treatment system on the overall process operation in these two runs was in the increased lime requirements (for ultimate neutralization of sulfuric acid added to the system). There were no adverse effects on calcium utilization, soluble calcium levels, or properties of solids generated in the absorbent regeneration reactor. In all of these respects, the performance of the system was consistent with that of a concentrated mode dual alkali process without sulfuric acid treatment.

The consumption of lime, however, rose significantly. In run 016 where the SO_2 removal equaled 2,050 ppm, sulfite oxidation throughout the system amounted to about 570 ppm, or 28% of the SO_2 removal. Approximately half of this oxidation rate was sustained by sulfate precipitation in the lime reactor and by soluble sulfate losses in the waste cakes. The remainder, about 14% of the SO_2 absorbed, was removed in the sulfuric acid reactor. Since the reactor efficiency averaged 0.57 (efficiencies ranged from 0.52 to 0.64), the sulfuric acid requirement amounted to about 26% of the SO_2 absorbed. This acid feed was directly reflected in the required increase of 26% in the lime feed (1.33/1.06 = 1.26). At the lower SO_2 inlet level of run 017, the use of sulfuric acid increased markedly due primarily to oxidation in the dual alkali system being a higher percentage of the SO_2 absorbed. In addition, Na_2SO_4 was used to make up lost sodium value. The combined oxidation and sulfate addition resulted in an increase in the lime feed of 80-85% over that required for SO_2 removal alone; and a total sulfuric acid requirement of 63% of the SO_2 removed.

It is clear from the pilot plant results that the sulfuric acid treatment scheme is a technically feasible and reliable approach to the removal of soluble sulfate from dual alkali systems. Because the use of this sulfuric acid treatment scheme may be costly when applied to systems with high oxidation rates (>40% of ΔSO_2) due to the sulfuric acid and extra lime requirements, it may be more appropriate for systems with intermediate levels of oxidation where the rate of sulfate formation cannot be easily handled in a simple concentrated active sodium mode.

Composite Diagram of Projected Pilot Plant Operations

Figure V-6 summarizes the operational characteristics of the various dual alkali process sections for the concentrated lime mode operation with sulfuric acid slipstream treatment for a high SO_2 inlet condition. This composite is based upon pilot plant operations and is analogous to the block diagrams provided in Chapter IV, Section C for the simple concentrated lime mode. Figure V-6 indicates the various inputs and outputs expressed in terms of SO_2 absorbed for a dual alkali system with an overall oxidation rate equivalent to 30% of the SO_2 absorbed. For each of the four process sections, the observed rates of sulfite oxidation and/or active sodium regeneration are also expressed as a function of SO_2 absorption.

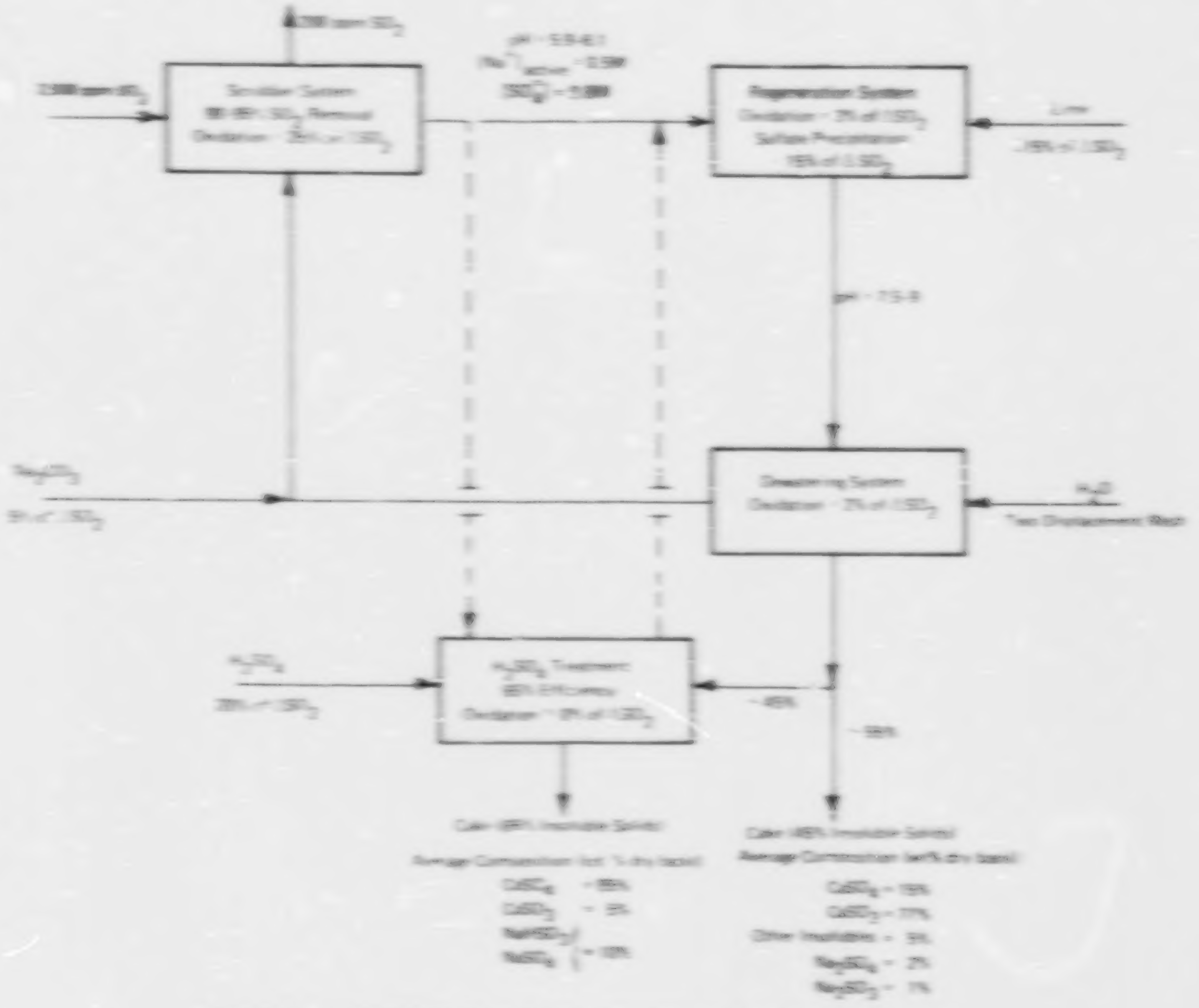

2300 ppm SO$_2$
230 ppm SO$_2$
Scrubber System
90-95% SO$_2$ Removal
Oxidation ~25% of ΣSO$_2$
pH ~ 5.9-6.1
[Na$^+$]$_{active}$ ~ 0.5M
[SO$_4^=$] ~ 0.5M
Regeneration System
Oxidation ~2% of ΣSO$_2$
Sulfate Precipitation
~15% of ΣSO$_2$
Lime
~95% of ΣSO$_2$
pH ~ 7.5-8
Dewatering System
Oxidation ~2% of ΣSO$_2$
H$_2$O
Two Displacement Wash
Na$_2$CO$_3$
5% of ΣSO$_2$
H$_2$SO$_4$ Treatment
85% Efficiency
Oxidation ~1% of ΣSO$_2$
H$_2$SO$_4$
20% of ΣSO$_2$
~45%
~55%
Cake 60% Insoluble Solids
Average Composition (wt % dry basis)
CaSO$_4$ ~85%
CaSO$_3$ ~ 5%
NaHSO$_3$/Na$_2$SO$_4$ ~10%
Cake 48% Insoluble Solids
Average Composition (wt% dry basis)
CaSO$_4$ ~ 15%
CaSO$_3$ ~ 77%
Other Insolubles ~ 3%
Na$_2$SO$_4$ ~ 2%
Na$_2$SO$_3$ ~ 1%

FIGURE V-4 COMPOSITE PILOT PLANT OPERATION – H$_2$SO$_4$ TREATMENT MODE

C. SULFURIC ACID REACTOR MODEL

A model of the sulfuric acid reactor system was developed to simulate the effects of various dual alkali process conditions on the sulfuric acid system efficiency. The principal purpose of the model was to provide a method for estimating reasonable sulfuric acid reactor operating conditions and for determining the sulfuric acid requirements in different dual alkali system applications. The model is described in detail in Appendix D.

As developed, the model applies to the operation of the reactor in the $CaCO_3$ limited regime. It is based upon the reaction equations discussed in Section A of this chapter, and assumes that chemical equilibrium is achieved in the system. The model determines the amount of sulfuric acid required to neutralize all alkalinity values in the slurry feed and adjust the pH into the 2.5 to 3.5 range. The levels of sulfate and calcium in solution in the reactor effluent are determined from an estimate of the apparent solubility product, K_{sp}', for $CaSO_4$ ($K_{sp}' = [Ca^{++}] \times [SO_4^{=}]$ with concentrations in mole/liter). The value of K_{sp}' used is the average of those values calculated from the laboratory data for the range of ionic strengths expected in the pilot plant operations. Since K_{sp}' is an input to the model, this can be adjusted for any desired ionic strength.

In order to adjust for pH, it has simply been assumed that enough sulfuric acid is added to convert up to 20% of the system TOS to H_2SO_3, depending upon the operating pH. This range of H_2SO_3 concentrations roughly corresponds to data obtained in the laboratory. It would, of course, be possible to try to determine the H_2SO_3/HSO_3^- ratio from the pH for H_2SO_3. However, very little data exist which will allow for reasonable estimates of the reference activity coefficients for the H_2SO_3 and HSO_3^- species at ionic strengths greater than 1.0. Furthermore, initial tests with the model indicate that calculated reactor efficiencies were relatively insensitive to rather large changes in this pH adjustment factor.

No consideration has been specifically given in the model to the formation of HSO_4^-. At the pH's involved, the amount of HSO_4^- should be less than a few percent of the total S(VI) species.

While this model proved adequate for determining the desired range of operating conditions for pilot plant testing and even, in most cases, predicting the pilot plant results, it was limited and a more general model was later developed. This later model was based upon estimates of the equilibrium composition of the reactor effluent liquor using the method of Kusik and Meissner[7] to predict activity coefficients of the appropriate species. This later model is described in Appendix D.

Model Application

The model has been used primarily to design pilot plant experiments and to determine the sulfuric acid requirement for various dual alkali system oxidation rates.

Table V-4 compares the experimental reactor efficiencies from the pilot plant operations with those predicted by the model. The model tracks the experimental runs fairly closely and, in most cases, the predicted value of efficiency is within about 15% of that observed. This agreement is good, particularly in light of the sensitivity of the model to the solids level in the feed slurry. A change of 10% in the solids level (from 20% to 22% solids) changes the efficiency estimate by about 30% (from say 40% to 52%). Since the solids level is an experimentally determined value that can vary slightly during a run, this sensitivity is significant.

The effects of other operating conditions on the reactor efficiency tend to be less than total insoluble solids, with small changes in [OH⁻], [TOS] and $CaCO_3$ in the cake generally producing small changes in efficiency. However, this does not mean that the sulfuric acid reactor efficiency is not sensitive to the levels of these alkaline species; rather it means that reasonably close estimates of their levels in the slurry feed are adequate for assessing/predicting reactor efficiency. The impact of large concentrations of available alkali (either in the solids or liquid) is illustrated in Figure V-5 in which the model's prediction of reactor efficiency is plotted as a function of lime utilization. In order to ensure 30% reactor efficiency under reasonable system operating conditions, calcium utilization in the absorbent regeneration system must exceed 75%; and to achieve 50% reactor efficiency, calcium utilization must exceed 90%.

The effect of changes in sulfate concentration also tends to be small, although the effect is a function of the actual level of sulfate. As sulfate concentrations in the feed decrease toward the equilibrium effluent sulfate concentrations, changes in sulfate concentration become more important.

Neither the pH adjustment factor nor the value of K_{sp}' was found to have a strong influence on the model performance over most of the range of operating pH's and solution compositions tested. A 100% increase in K_{sp}' from 8×10^{-5} to 16×10^{-5} generally decreases the predicted reactor efficiency by less than 10%. Similarly a 50% increase in the pH adjustment factor, from 0.2 to 0.3, usually decreases the efficiency prediction by about 5%.

D. CONCLUSIONS

The sulfuric acid slipstream treatment scheme is a technically feasible and reliable approach for removal of soluble sulfates from dual alkali systems. The treatment produces sulfate in the form of gypsum that can be readily dewatered to 65 wt % insoluble solids or higher. The scheme adds complexity to any dual alkali mode to which it is applied. The complexity is reflected in additional capital costs and in increased operating costs for the sulfuric acid, the additional lime consumed and the additional solid waste produced.

The amount of sulfuric acid required is important since it directly affects the overall lime requirement. As the sulfuric acid addition rate increases, the lime rate must increase accordingly for precipitation of the additional

TABLE V-6 MODEL SIMULATIONS OF PILOT PLANT OPERATIONS

Feed Ratio $\left(\frac{\text{mols Na}_2\text{SO}_4}{\text{mol CaSO}_4}\right)$	Experimental Reactor Efficiency	Efficiency Predicted By Model
0.54	0.68	0.72
0.57	0.61	0.56
0.60	0.43	0.65
0.67	0.39	0.43
0.75	0.22	0.13
0.76	0.28	0.19
0.95	0.10	-0.12

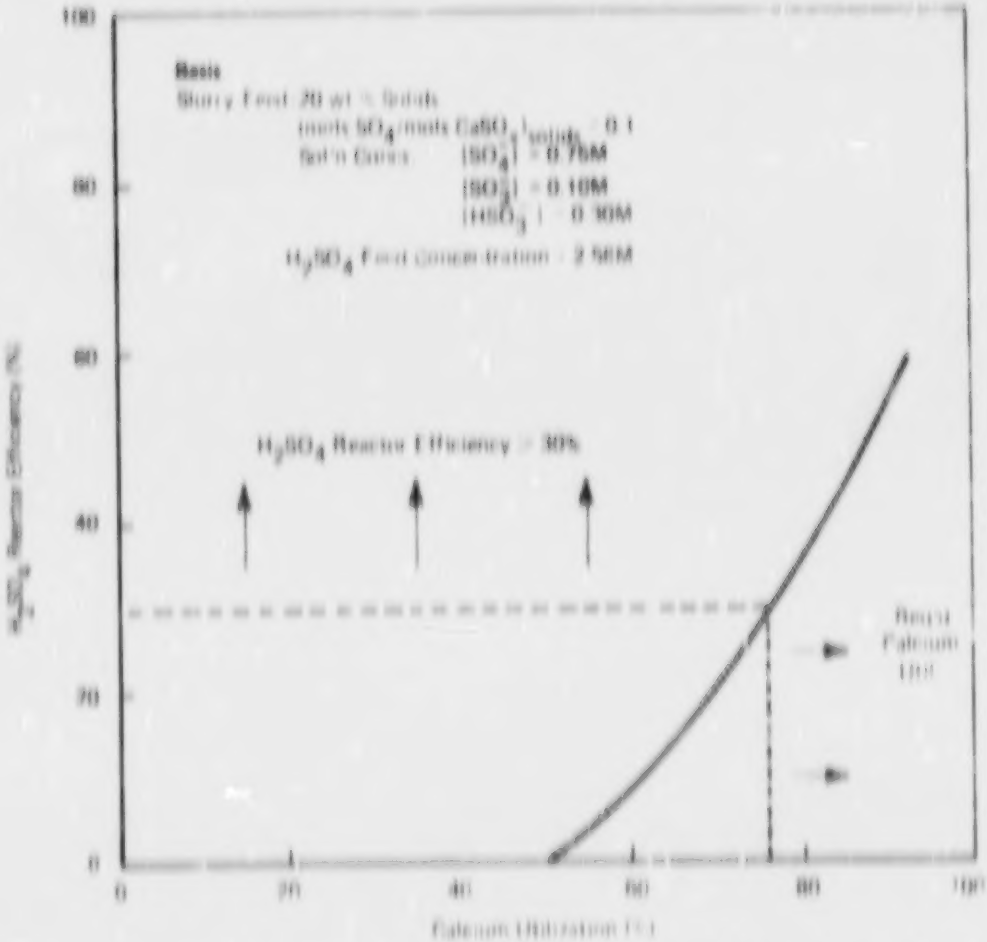


FIGURE V-5 H_2SO_4 REACTOR EFFICIENCY VERSUS CALCIUM UTILIZATION sulfur value added to the system. The maximum efficiency of the treatment scheme ((mols Na_2SO_4 removed/mols H_2SO_4 fed) x 100%) appears to be practically limited to a maximum in the range of 60-70%. In order to precipitate sulfate at a rate sufficient to keep up with an oxidation rate of 15% (of the SO_2 absorbed), the lime feed requirement will be increased by 25% for a 60% reactor efficiency.

The efficiency of the sulfuric acid treatment is importantly affected by the calcium utilization achieved in the absorbent regeneration reactor in the main dual alkali loop. As calcium utilization decreases in the main loop the efficiency of the sulfuric acid slipstream treatment decreases and acid consumption increases to neutralize unreacted lime in the filter cake. In order to achieve a 50% efficiency in the sulfuric acid treatment system, calcium utilization in the main dual alkali loop must exceed 90%.

Because the use of this sulfuric acid treatment scheme may be costly when applied to systems with high oxidation rates (due to the sulfuric acid and extra lime requirements), it may be more appropriate for systems with intermediate levels of oxidation where the rate of sulfate formation cannot be easily handled in a simpler concentrated sodium mode. The consequences of using the sulfuric acid slipstream treatment approach for sulfate regeneration should, therefore, be carefully evaluated in terms of the overall process operation. In many cases, where oxidation rates are high enough that they cannot be easily handled by normal concentrated mode operation, other dual alkali approaches, such as the dilute lime system described in Chapter VII, might be more promising than a sulfuric acid treatment alone.

VI. LIMESTONE REGENERATION -- CONCENTRATED MODE

A. INITIAL LABORATORY STUDIES

In view of the increasing cost of the energy required to calcine limestone to lime, operating cost savings would be realized if limestone could be used directly in a dual alkali process in lieu of lime. Limestone has been used in FGD systems which employ direct slurry scrubbing, and the chemical equilibria involved have been characterized extensively. By analogy, limestone should be applicable to dual alkali regeneration. However, because there are significant differences between reaction conditions in direct slurry scrubbing and dual alkali regeneration -- one of the most important is the significantly higher ionic strengths found in concentrated dual alkali solutions -- a program of laboratory experiments was undertaken to study the reaction between limestone and concentrated sodium sulfite/bisulfite solutions. In a parallel effort, the use of limestone to regenerate dilute sodium sulfite/bisulfite solutions was studied by personnel at the Research Triangle Park laboratories of the EPA. The results of those studies are discussed in Chapter VII.

Limestone is being used in two commercial dual alkali systems in Japan. However, both systems utilize special treatment steps for sulfate precipitation; both ultimately produce gypsum and are relatively complex processes. They are described in more detail in a paper by Kaplan.[3]

The ADL laboratory program consisted of an initial series of batch experiments in which the effects of the type of limestone, limestone feed stoichiometry, reaction temperature, and sodium sulfate level on the kinetics and equilibria of the reaction were studied. In subsequent continuous stirred-tank reactor (CSTR) experiments, limestone utilization and the physical properties of the product solids were studied as a function of a number of experimental variables.

Limestone will not react with sodium sulfite solutions to produce calcium sulfite since limestone is less soluble than the calcium sulfite and does not dissolve sufficiently to react. The bisulfite ion, HSO_3^-, however, is sufficiently acidic to react with limestone. This neutralization reaction, which results in the ultimate precipitation of calcium sulfite, can be written simplistically as follows:

$$CaCO_3(s) + 2NaHSO_3 \rightarrow CaSO_3(s) + Na_2SO_3 + H_2O + CO_2 \uparrow (g)$$

In fact, the bisulfite initially present is never completely neutralized because at pH's where the reaction will proceed (up to about pH = 7), the species H_2CO_3, HCO_3^-, HSO_3^-, and $SO_3^=$ all exist in significant quantities in equilibrium with one another. Nevertheless, based on the above equation one can express the amount of limestone fed as the percent of the stoichiometric amount which would be required to neutralize the HSO_3^- initially present.

$$\% \text{ Stoich} = \left(\frac{\text{mols } CaCO_3}{0.5 \times \text{mols } HSO_3^-} \right) \times 100\%$$

Thus, a feed stoichiometry of 100% is obtained when the mol ratio of $CaCO_3$ to HSO_3^- fed is 1:2. This definition of feed stoichiometry will be used throughout the discussion which follows.

Regardless of the nature of the species in solution, it is the removal of soluble sulfur-containing ions -- both sulfur (IV), sulfite, and sulfur (VI), sulfate -- from solution as insoluble calcium salts by which the effectiveness of limestone utilization is realistically evaluated. In CSTR experiments, utilization was based on analyses of the reactor product solids and calculated as follows:

$$\% \text{ Utilization} = \left(\frac{\text{mols } CaSO_x \text{ in solids}}{\text{total mols Ca in solids}} \right) \times 100\%$$

1. Batch Studies Comparing the Reactivities of Different Limestones

Since the initial batch experiments were comparative in nature, for the sake of expediency the precipitation of $CaSO_4$ was ignored and limestone utilization was computed on the basis of the decrease in the concentration of soluble sulfur (IV) -- total oxidizable sulfur, TOS -- in solution as the reaction proceeded. Thus, if limestone is fed at 100% of stoichiometry and it is completely utilized, one would expect [TOS] to decrease by an amount equal to one-half the concentration of bisulfite ion, $[HSO_3^-]$, initially present. This relationship can be expressed as follows:

$$\% \text{ Utilization} = \left(\frac{\text{TOS in} - \text{TOS out}}{0.5 \times HSO_3^- \text{ in} \times (\% \text{ Stoich}/100)} \right) \times 100\%$$

Because the formation of $CaSO_4$ is ignored in this calculation, its use leads to conservative estimates of actual utilization.

The initial experiments in the laboratory program compared the relative reactivities of several types of limestone toward concentrated, acidic sodium sulfite/bisulfite solutions. In previous studies related to limestone slurry scrubbing, Drehmel[10] found significant differences in reactivity which were attributed to differences in both the chemical and physical properties of the wide variety of limestones tested.

Materials from three sources were available in quantity for testing and subsequent use in this laboratory program. By chemical analysis all were more than 95% $CaCO_3$. The materials included:

- Reagent grade $CaCO_3$ (precipitated chalk); Fisher Scientific Company.

- A natural calcite obtained from Pfizer, MPM Division, Clifton, New Jersey. This material (Marblewhite 200) was an industrial grade, low magnesium limestone produced at Adams, Massachusetts.

- Fredonia limestone ground by and obtained from the EPA/TVA Shawnee Test Facility.

Based on the sieve analyses shown below, the Marblewhite 200 and the Fredonia limestones appeared to be similar in their particle size distributions while the reagent $CaCO_3$ was uniformly finer.

	Limestone Type		
Mesh	**Reagent**	**Marblewhite 200**	**Fredonia**
- 300	100%	87.5%	85.7%
-200 + 300	-	11.0%	8.9%
-100 + 200	-	1.5%	3.7%
- 60 + 100	-	0.2%	0.4%

Examination under the scanning electron microscope (SEM) revealed more subtle differences which were not evident from the sieve analysis. The reagent grade material was composed of quite uniformly sized cubes about 8 microns (µ) on a side. The Marblewhite particles also appeared crystalline but were very irregular and jagged in shape with a longest dimension ranging from 2 µ to greater than 50 µ; an average length was estimated to be about 20 µ. The Fredonia material, which was similar to Marblewhite by sieve analysis, appeared very different under SEM examination. It appeared amorphous; the bulk of the particles were rough, irregular spheres about 2-8 µ in diameter. Particles larger than 10 µ were present but they appeared to be agglomerates of many smaller particles.

The results of batch reactions of the three limestones with sodium sulfite/bisulfite/sulfate solutions at 50°C are shown in Figure VI-1. The progress of the reaction as a function of time was followed by measuring the decrease in TOS concentration in solution. The substantially higher reactivity of Fredonia limestone (as compared to reagent $CaCO_3$) is immediately evident from the more rapid TOS reduction obtained with the Fredonia material. The solution with which the Marblewhite was reacted had a somewhat higher initial TOS level than the other two solutions.

To permit a better comparison of reactivity, initial reaction rates were computed and the values included in Figure VI-1. The overall reaction rates shown are the change in TOS concentration per minute for the reaction time period, 0-15 minutes. The computed overall reaction rates for

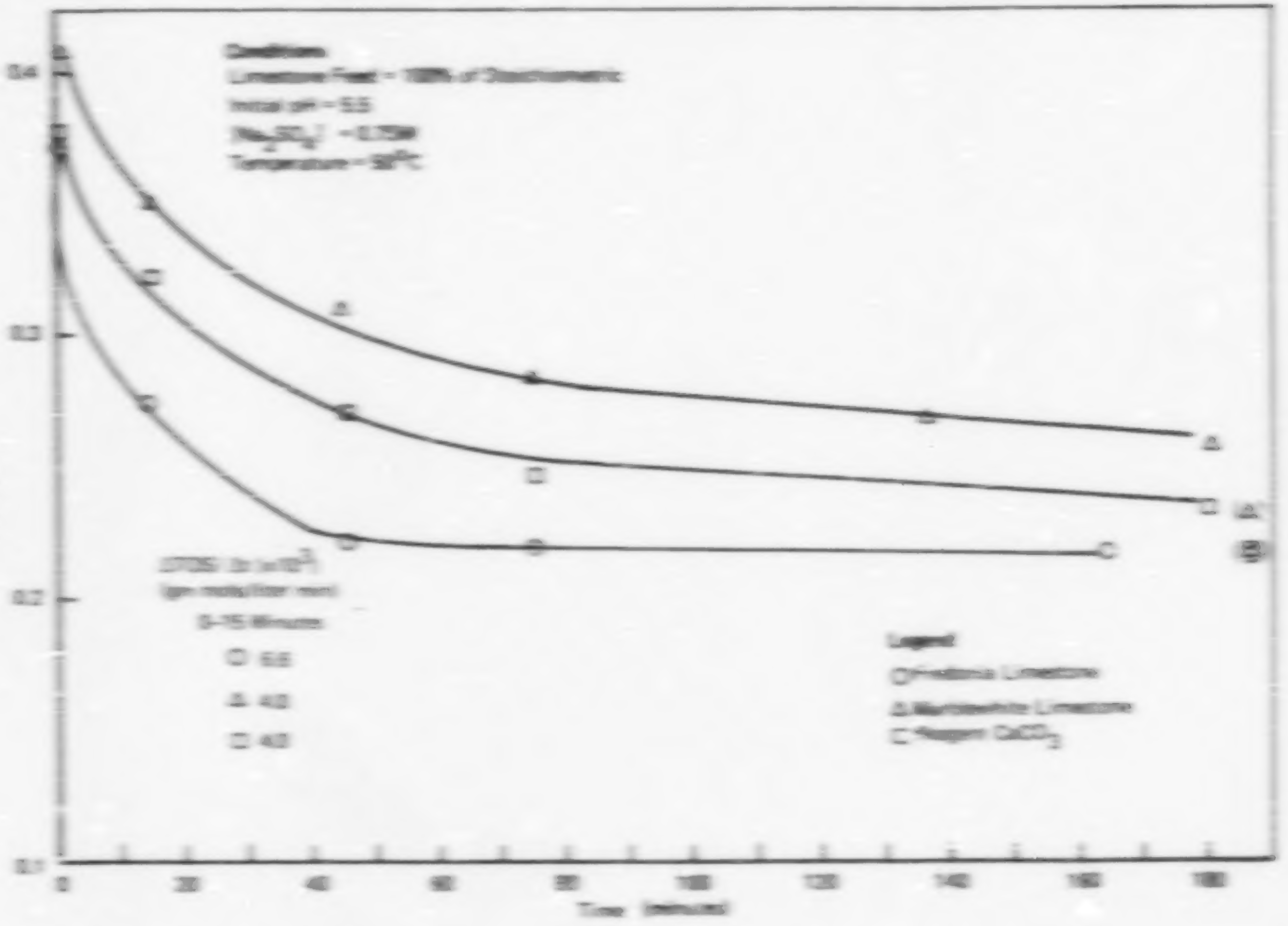


FIGURE VI-1 COMPARISON OF LIMESTONE REACTIVITIES IN BATCH REACTIONS

Marblewhite limestone and reagent $CaCO_3$ were essentially the same while the rate observed for Fredonia limestone was about 50% faster than that of either of the other two limestones.

With the Fredonia limestone, TOS changed very little after the first 45 minutes of reaction. With the other two materials, a noticeable reduction in TOS, indicative of continuing slow reaction, was observed throughout the remainder of the experiments which were terminated after three hours.

Plotted at the extreme right-hand side in parentheses in Figure VI-1 are the TOS levels which would have been obtained if the limestone which was fed had been completely utilized to precipitate calcium sulfite. The final TOS level observed for Fredonia limestone was much closer to the theoretical level than it was for the other two materials. Utilizations, based on TOS reduction, in solution, even after three hours of reaction, were markedly poorer for Marblewhite limestone and reagent $CaCO_3$ (81% and 85%, respectively) than for the Fredonia material (96%). Utilization of the Fredonia material after only 45 minutes of reaction was about 92%, whereas utilizations of Marblewhite and reagent $CaCO_3$ after 45 minutes were only 54% and 64%, respectively. If precipitation of $CaSO_4$ had been taken into account, all utilizations would have been higher; in the case of Fredonia, utilization would have been about complete.

Because of the chemical similarity of all three materials, the observed difference in their reactivity probably resulted from the fact that the Fredonia limestone consisted of amorphous particles with a higher accessible surface area than the crystalline particles characteristic of the other two.

Because of its significantly higher reactivity in batch tests, the Fredonia limestone was used almost exclusively in the remainder of the batch and CSTR experiments that were performed. We do realize, however, that further consideration must be given to the effect of limestone reactivity before a complete assessment of its potential for dual alkali regeneration in a wide variety of situations can be made. The batch reaction method employed seems to be a relatively simple but realistic means to study reactivities.

2. Effects of Feed Stoichiometry, Sulfate Concentration, and Temperature on Reaction Rate

The effect of changing the Fredonia limestone feed stoichiometry on the rate of the regeneration reaction at 50°C is shown in Figure VI-2. When the amount of limestone fed was reduced from 100% to 50% of the stoichiometric amount required to neutralize the HSO_3 initially present, the reaction rate during the first 15 minutes of reaction also decreased significantly, although the percent decrease in reaction rate was not as great as the reduction in the feed stoichiometry. The theoretical minimum TOS level after 45 minutes of reaction was more closely approached

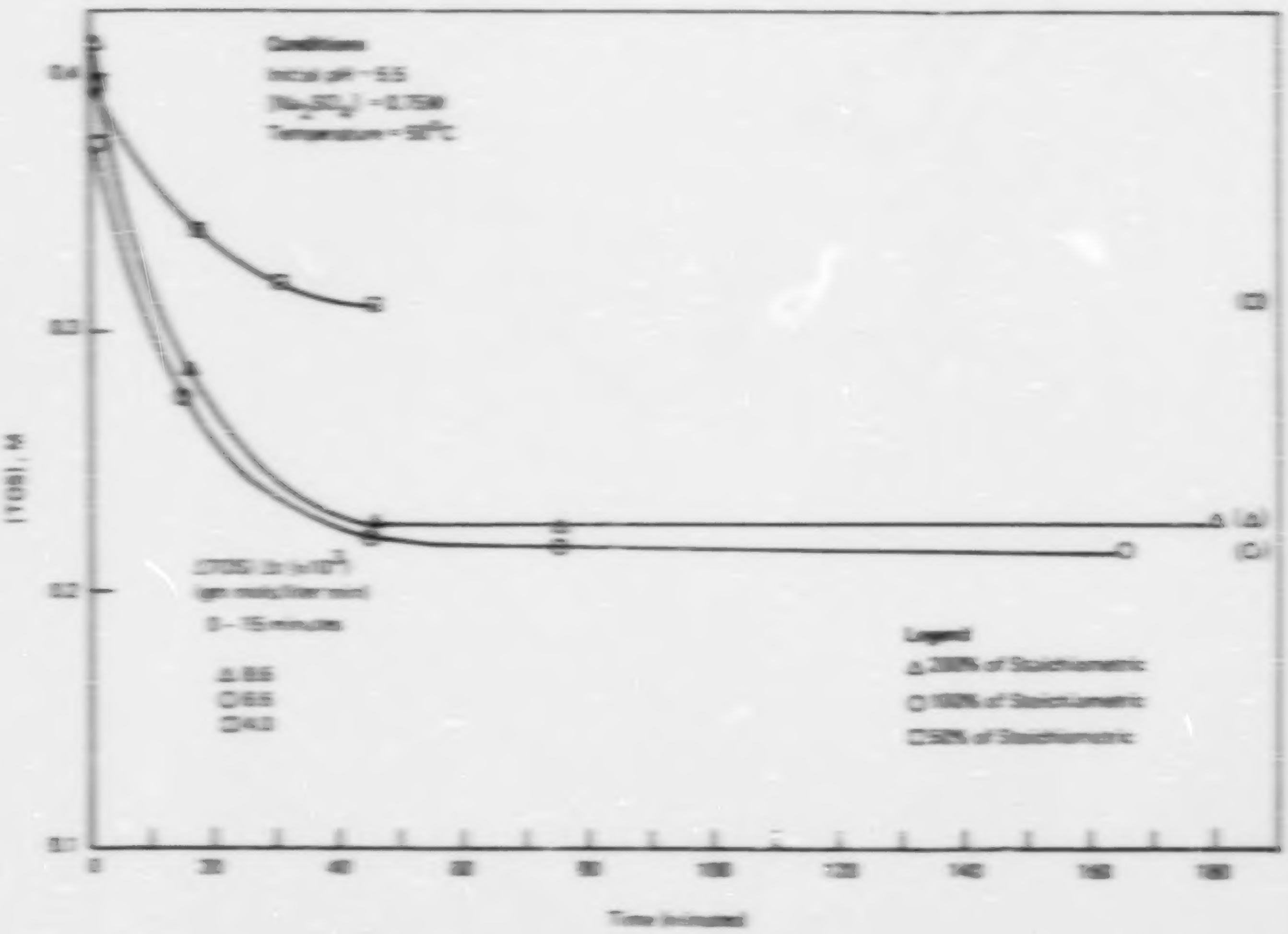


FIGURE VI-2 EFFECT OF LIMESTONE FEED STOICHIOMETRY ON REGENERATION RATE WITH FREDONIA LIMESTONE

at the lower (50%) stoichiometry, and the resulting limestone utilization (based on TOS reduction only) was about 97% as compared to 92% when the feed was 100% of stoichiometric. When the limestone feed stoichiometry was doubled from 100% to 200%, the initial reaction rate increased about 30% and the TOS concentration after 45 minutes had fallen essentially to the minimum theoretical level. Within experimental error, the concentration of TOS remained constant during the remainder of the experiment. However, none of the limestone added in excess of 100% stoichiometric reacted; the overall utilization was only about 50%.

The dependence of the reaction rate on limestone feed stoichiometry observed in these experiments indicates that limestone dissolution is one of the rate-limiting steps in the regeneration reaction with limestone.

The effect on reaction rate of the concentration of Na_2SO_4 in solution at 50°C is shown in Figure VI-5. It is immediately obvious that at 1.25M Na_2SO_4, the reaction was significantly slower than at the two lower Na_2SO_4 levels. Examination of the computed reaction rates for the initial 15 minutes of reaction reveals that initial rates were significantly different for each of the Na_2SO_4 levels studied. Each increase in the concentration of Na_2SO_4 was accompanied by a corresponding decrease in initial reaction rate. The reaction rate for the first 45 minutes was essentially the same for Na_2SO_4 levels of 0.25M and 0.75M, but the corresponding rate at 1.25M Na_2SO_4 was still significantly lower.

All of the preceding experiments were conducted at a temperature of 50°C which is representative of the temperature at which a reactor would operate if scrubber effluent were neither heated nor cooled prior to regeneration. The significant decrease in reaction rate at a lower temperature, 38°C, is shown in Figure VI-6. The 12°C reduction in reactor temperature produced essentially the same reduction in the calculated reaction rate as did increasing the concentration of Na_2SO_4 from 0.75M to 1.25M in the preceding experiment.

3. Continuous Reactor Studies of Regeneration with Limestone

The results of the batch experiments indicated that Fredonia limestone could be used effectively to regenerate concentrated sodium bisulfite/sulfite solutions. The regeneration with limestone was studied further in the laboratory CSTR (continuous, stirred tank reactor) to observe the physical properties of the solids produced, to ascertain whether or not sulfate would also be precipitated during the course of the reaction, and to obtain a more realistic estimate of achievable limestone utilization.

The results of the batch experiments indicates that with Fredonia limestone, achieving nearly complete utilization at a temperature of 50°C and with Na_2SO_4 concentrations of 0.75M or less, required 45 minutes of

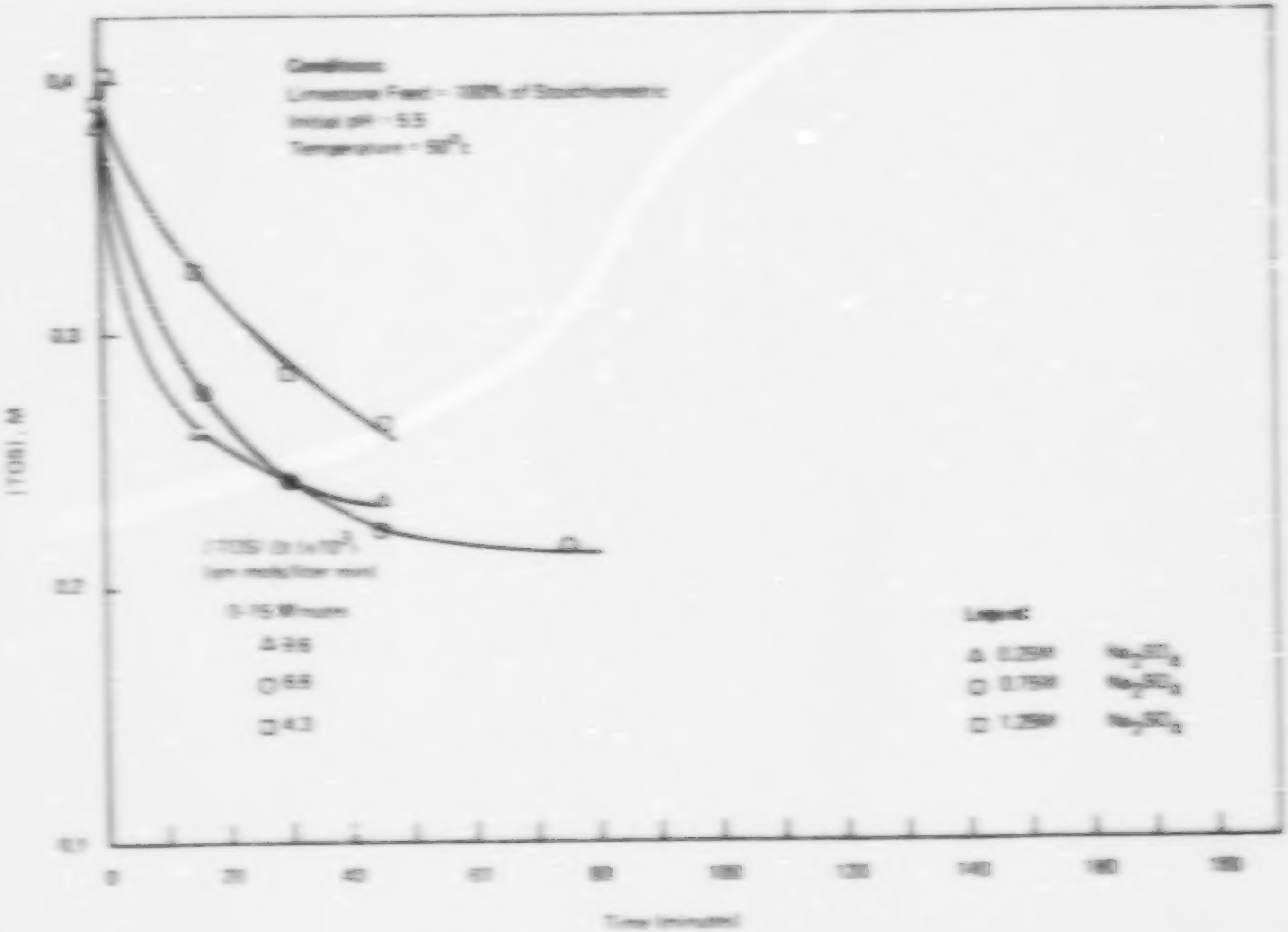


FIGURE VI-2 EFFECT OF Na_2SO_4 CONCENTRATION ON REGENERATION RATE WITH FREDONIA LIMESTONE

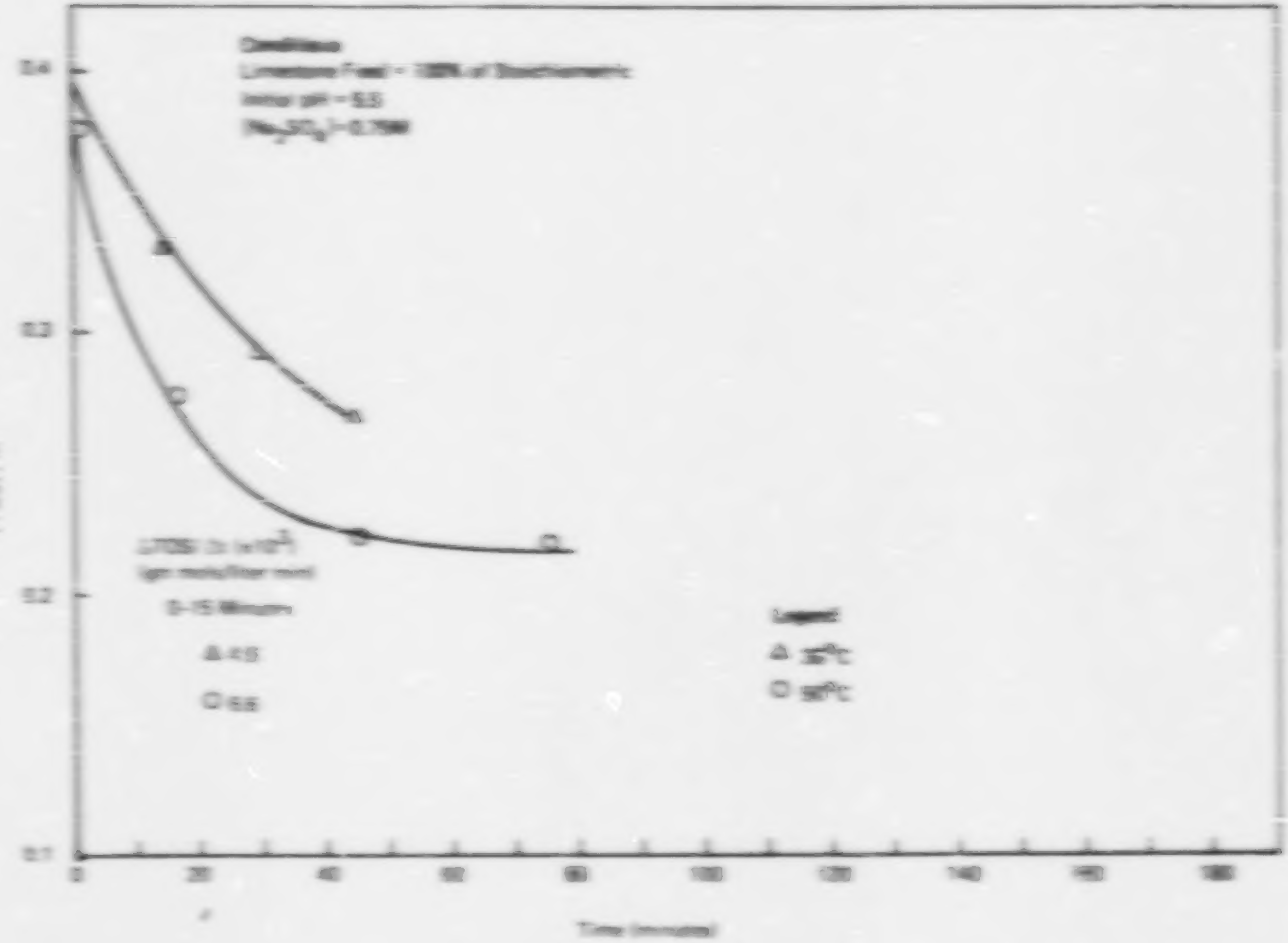


FIGURE VI-4 EFFECT OF TEMPERATURE ON REGENERATION RATE WITH FREDONIA LIMESTONE

batch reaction time. Assuming a simple, second-order reaction overall, then in a CSTR, that extent of reaction would translate to a residence time of roughly 2-2.5 hours. However, the CSTR system available when these studies needed to be performed had been specifically designed to operate at shorter residence times (5-50 minutes) for studying regeneration with lime, and would not operate reliably at longer residence times. For the sake of expediency, an initial set of CSTR studies with limestone was performed at the 50 minute maximum residence time obtainable. A new, larger CSTR was constructed somewhat later and comparative runs at longer residence times were then carried out.

The observed utilizations of limestone (based on $CaSO_x$/total Ca in the product solids) in the CSTR experiments as a function of limestone feed stoichiometry are shown in Figure VI-5. Included for reference are the utilizations achieved after 45 minutes of batch reaction based on TOS removal only; the batch data are known to be somewhat low because $CaSO_4$ formation was not included. Even at the 50 minute CSTR residence time, utilizations of Fredonia limestone greater than 80% were achieved with a feed stoichiometry of about 50%. When the stoichiometric amount of limestone fed was increased, utilization decreased significantly.

Utilization of the less reactive Marblewhite limestone was also studied in the 50 minute CSTR at a feed stoichiometry of 100%. Utilization of this material was only about 55%; utilization of Fredonia under similar conditions was about 70%.

Included in Figure VI-5 are the results of a number of experiments in which the CSTR residence time was maintained at 50 minutes but a portion of the reactor effluent slurry was collected, filtered, and the solids recycled to the reactor. In once-through CSTR operation, the weight percent suspended solids in the reactor effluent slurry was typically about 2%. In several experiments with Fredonia limestone, the suspended solids level in the reactor was raised to about 5% by recycling solids, and, as shown in Figure VI-5, utilization of the limestone increased significantly over that observed for once-through operation. Operation with solids recycle also appeared to increase the utilization of Marblewhite limestone. The two experiments with Marblewhite were conducted at different feed stoichiometries, but when effluent solids were recycled, Marblewhite utilization was comparable to that obtained during once-through operation with Fredonia; in once-through operation, Marblewhite utilization had been significantly lower than that observed for Fredonia.

Recycling solids effectively increased the amount of time available for the limestone to react by a factor of 2.5-3. Increasing reactor residence time by the same factor produced essentially the same improved utilization as shown for the once-through 150 minute CSTR run.

The solids produced in the once-through CSTR experiments with Fredonia limestone were analyzed for their $CaSO_4$ content to ascertain whether or not sulfate was being precipitated during the course of the reaction. The amount of $CaSO_4$ found, rationed to the total $CaSO_x$ present in the

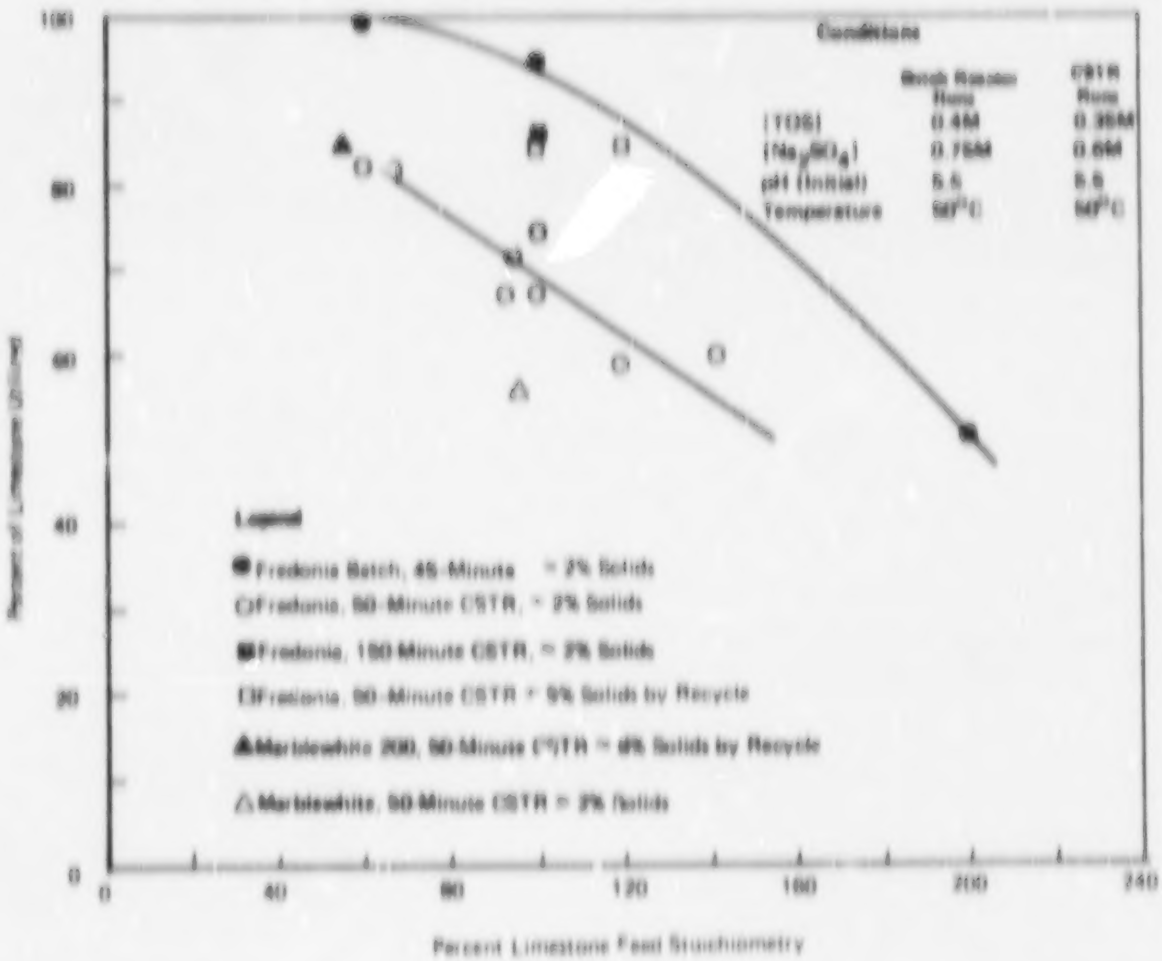


FIGURE VI-5 UTILIZATION OF TWO LIMESTONES IN BATCH AND CONTINUOUS REACTORS

solids, is shown as a function of the Na_2SO_4 concentration in the reactor in Figure VI-6. Significant amounts of sulfate precipitation were observed and were similar to the behavior observed when regenerating with lime. The sulfate precipitation increased linearly with increasing Na_2SO_4 concentration in the reactor solution. In fact, for a given Na_2SO_4 concentration, the actual sulfate precipitation with limestone was the same, within experimental error, as had been observed earlier for lime.

Because the matrix of CSTR experiments was limited in size, the sulfate precipitation shown in Figure VI-6 was obtained from experiments with differing limestone feed stoichiometries as indicated in the figure. The fact that no significant deviations from linear dependence on sulfate concentration were observed for the wide variations in feed stoichiometry, suggests that stoichiometry had little or no effect on sulfate precipitation when limestone was used.

Total dissolved calcium levels measured in the reactor effluent for the experiments shown in Figure VI-6 ranged from about 70-200 ppm, increasing with increasing Na_2SO_4 concentration. However, even at the highest sulfate levels studied, the solutions did not approach saturation with respect to gypsum. By X-ray diffraction, the only sulfur-containing crystalline phase which could be detected in numerous samples of product solids was $CaSO_3 \cdot 1/2H_2O$. These same two observations were made when regeneration with lime was studied. When taken together with the essentially identical dependence of sulfate precipitation on Na_2SO_4 concentration, they suggest that sulfate precipitation by lime and limestone occurs by the same mechanism, possibly involving the formation of some sort of solid solution of $CaSO_4$ in the $CaSO_3 \cdot 1/2H_2O$ lattice.

The solids produced in these initial CSTR experiments all exhibited settling behavior similar to that of "good settling material" previously produced in the laboratory and in the pilot plant when regenerating with lime.

B. SUBSEQUENT LABORATORY STUDIES OF FACTORS AFFECTING THE PHYSICAL PROPERTIES OF LIMESTONE PRODUCT SOLIDS

With the laboratory experimental results up to that time all indicating that Fredonia limestone could be used to regenerate concentrated sodium bisulfite/sulfite solutions effectively, two closed-loop tests with Fredonia limestone were attempted in the ADL pilot plant. In the first run, the limestone reactor was a simple CSTR with a 90 minute holdup; in the second run, the CSTR was operated with a recycle of solids from the thickener underflow. Although calcium utilizations ranged from 75% to 85%, the dewatering properties of the solids generated in the reactors were poor. Extremely low settling rates resulted in the carryover of a considerable amount of solids in the thickener overflow until the scrubber feed liquor contained 2-3 wt % solids. The filter cake reflected the poor quality of solids. The washed cake averaged less than 40 wt % solids (dry cake basis).

During operating periods when the reactor effluent slurry pH fell below 6.8, bubbling began to occur in the thickener, indicating that a significant

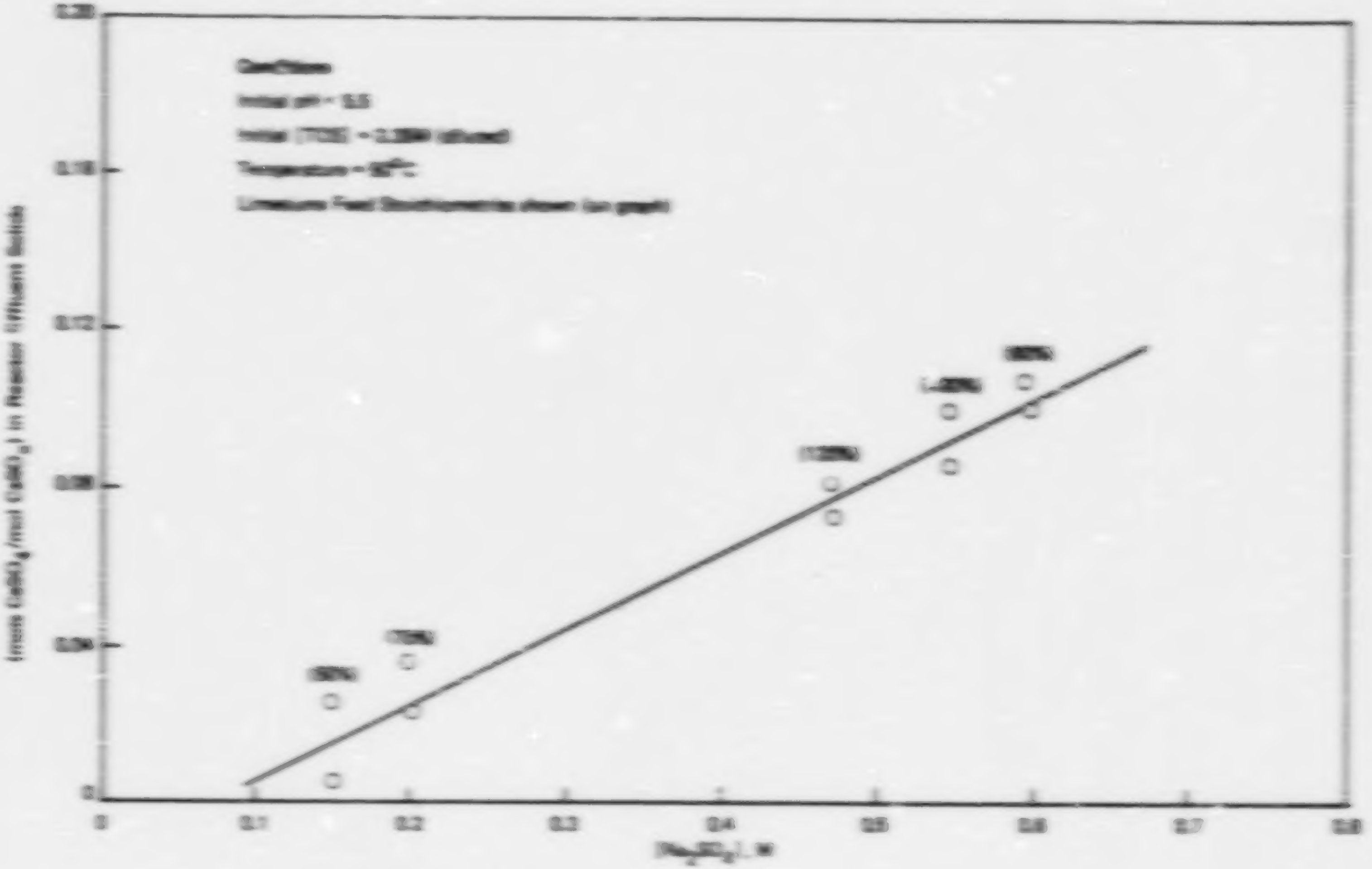


FIGURE VI-4 PRECIPITATION OF SULFATE BY FREDONIA LIMESTONE IN 60-MINUTE CSTR EXPERIMENTS

amount of additional reaction was taking place. This contributed to the solids carryover in the thickener overflow.

1. Effects of Sulfate Level on Settling Behavior of Solids

After those initial pilot plant experiences, laboratory studies with the seemingly negative goal of producing poor settling solids were undertaken in an effort to explain the pilot plant results. Three differences between operating conditions in the laboratory and in the pilot plant were explored.

First, limestone had been fed as a slurry in the laboratory but was fed dry in the pilot plant. A CSTR experiment was conducted in the laboratory with limestone fed dry and no deterioration of settling properties over those observed in previous laboratory studies could be detected.

Second, the simulated scrubber bleed solutions which were used in the laboratory studies did not contain dissolved CO_2. In the pilot plant, the scrubber effluent did contain dissolved CO_2 which could have impeded the reaction. However, good solids settling behavior was still observed when the solution fed to the laboratory CSTR was saturated with CO_2.

Third, during the pilot plant tests, the Na_2SO_4 concentration level ranged from 0.9M to 0.8M. The highest Na_2SO_4 level fed to the laboratory CSTR up to that time had been 0.75M which, after dilution by the limestone slurry, resulted in a maximum Na_2SO_4 concentration of 0.6M in the reactor. Subsequent laboratory CSTR experiments at higher concentrations of Na_2SO_4 indicated that the higher Na_2SO_4 level in the pilot plant was probably at least one factor responsible for the poor settling behavior observed.

The dramatic changes in the settling behavior which occurred when the concentration of Na_2SO_4 in the laboratory CSTR was changed from 0.6M to 1.0M are shown in Figure VI-7. (Here, the "meniscus position" indicates the position of the clear liquor/slurry interface, or the volume to which the solids slurry settles, starting with 100 ml of slurry in a 100 ml graduated cylinder.) At intermediate concentrations of Na_2SO_4 (0.75-0.80M), the settling behavior observed, for samples taken one hour after the reactor had filled and begun to overflow, was between the two extremes. At intermediate Na_2SO_4 levels, it was further observed that settling behavior tended to improve and approach that observed for 0.6M Na_2SO_4 as the reactor was allowed to continue to operate for an additional period of 2-3 hours. However, the very poor settling behavior observed at the highest Na_2SO_4 concentration did not change over a period of several hours of reactor operation.

2. Effects of Magnesium on the Limestone Regeneration Reaction

Having observed the dramatic effect that a change in Na_2SO_4 level could have on the regeneration reaction when it was operated under otherwise constant conditions, it was decided that the effect of other extraneous

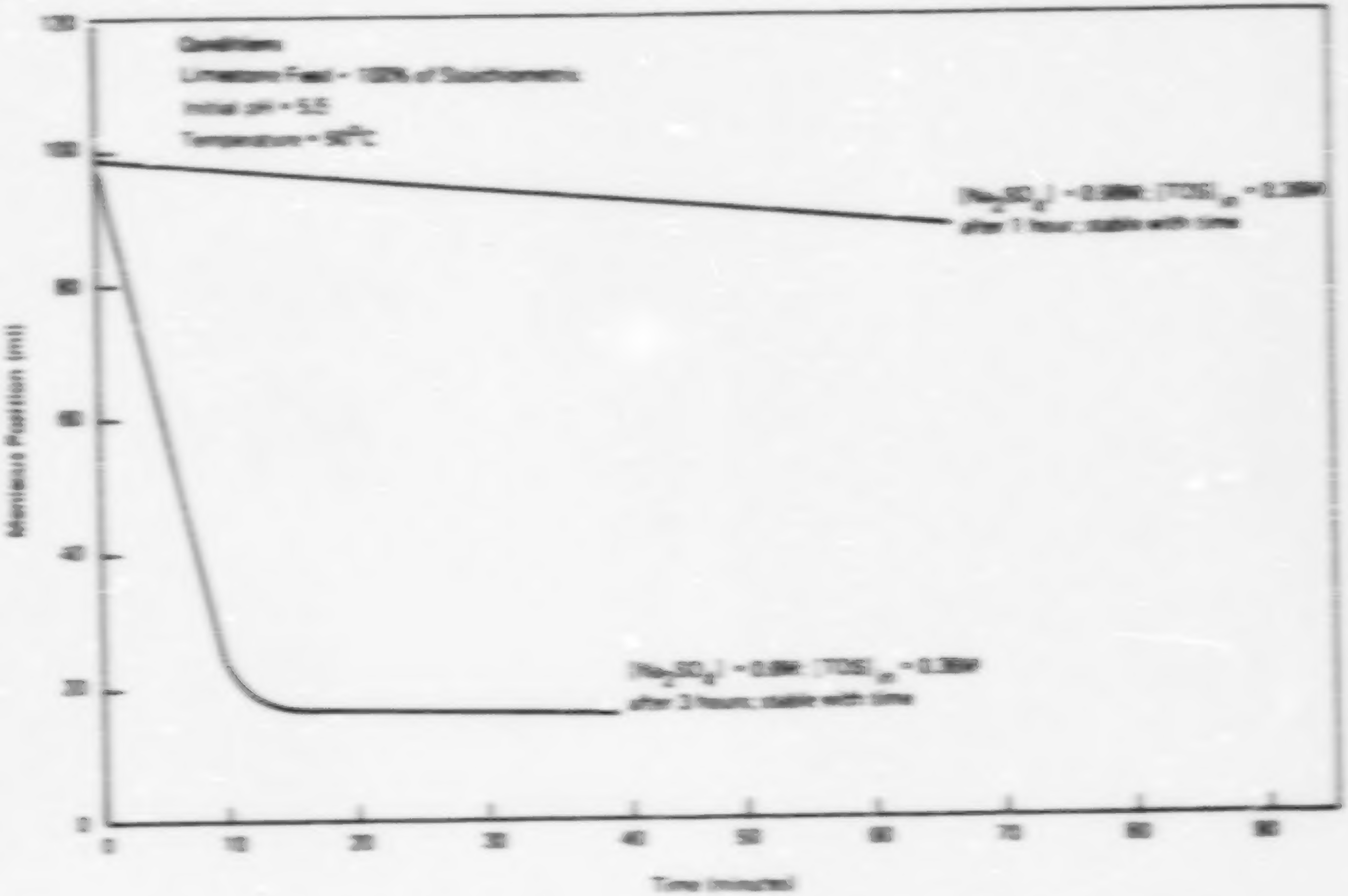


FIGURE VI-7 SETTLING CURVES FOR SOLIDS PRODUCED IN 50-MINUTE CSTR EXPERIMENTS USING FREDONIA LIMESTONE

species on the regeneration reaction should be studied. Limestone can contain varying amounts of magnesium; chlorides can be absorbed from flue gases; iron can be corroded by process equipment; and other soluble species might build up to significant levels during extended periods of closed-loop operation. The effects of magnesium were studied in detail in this program.

The effect of magnesium, added as $MgSO_4$, at a concentration of 200 ppm (mg/liter) on the reaction of Fredonia limestone in a batch experiment is shown in Figure VI-8, where TOS precipitation as a function of time with and without the added magnesium is compared. The 200 ppm of Mg^{++} reduced the reaction rate significantly. In fact, if the calculated initial reaction rates observed with 200 ppm Mg^{++} present are compared with those shown in Figure VI-3 when the Na_2SO_4 level was increased to 1.25M, it can be seen that the presence of the small amount of magnesium slowed the reaction more than increasing the Na_2SO_4 level from 0.75M to 1.25M.

The settling behavior of solids produced during 50 minute CSTR experiments in which about 100 ppm and 200 ppm of Mg^{++} had been added to the solution to be regenerated is shown in Figure VI-9. Settling curves for experiments in which no $MgSO_4$ was added are included for comparison. The 19 ppm and 24 ppm Mg^{++} levels shown in Figure VI-9 for these experiments were the amounts of magnesium dissolved from the limestone.

The significant change in settling behavior when Mg^{++} was added can be seen by comparing the settling curves (B, C and E) for the three experiments in which the concentration of Na_2SO_4 was held essentially constant at about 0.6M. The effects of Na_2SO_4 and Mg^{++} levels in solution appeared to be similar and, after a fashion, additive. When the concentration of Na_2SO_4 was reduced to 0.43M (curve D), moderately good settling behavior was observed even with 208 ppm Mg^{++} present.

Since, in earlier tests in which magnesium was not intentionally added to the scrubber bleed, it had been shown that a significant improvement in limestone utilization could be realized by increasing the CSTR residence time from 50 minutes to 120-150 minutes, it was of immediate interest to determine whether or not the deleterious effects of a few hundred ppm of magnesium would be more or less severe at a longer residence time. Experiment 65 was carried out, in which a simulated scrubber bleed containing about 300 ppm of soluble magnesium was regenerated with limestone in a 120 minute CSTR maintained at 50°C. The solids in the effluent slurry from that experiment settled quite well as shown in Figure VI-10. However, the rate at which the solids settled became slower for samples which were taken at later times during the experiment.

Since increasing the CSTR residence time seemed to improve markedly the poor settling behavior which had previously been observed when a few hundred ppm of magnesium was present, the level of soluble magnesium next was raised, in experiment 66, to 2,200 ppm, a level which might be

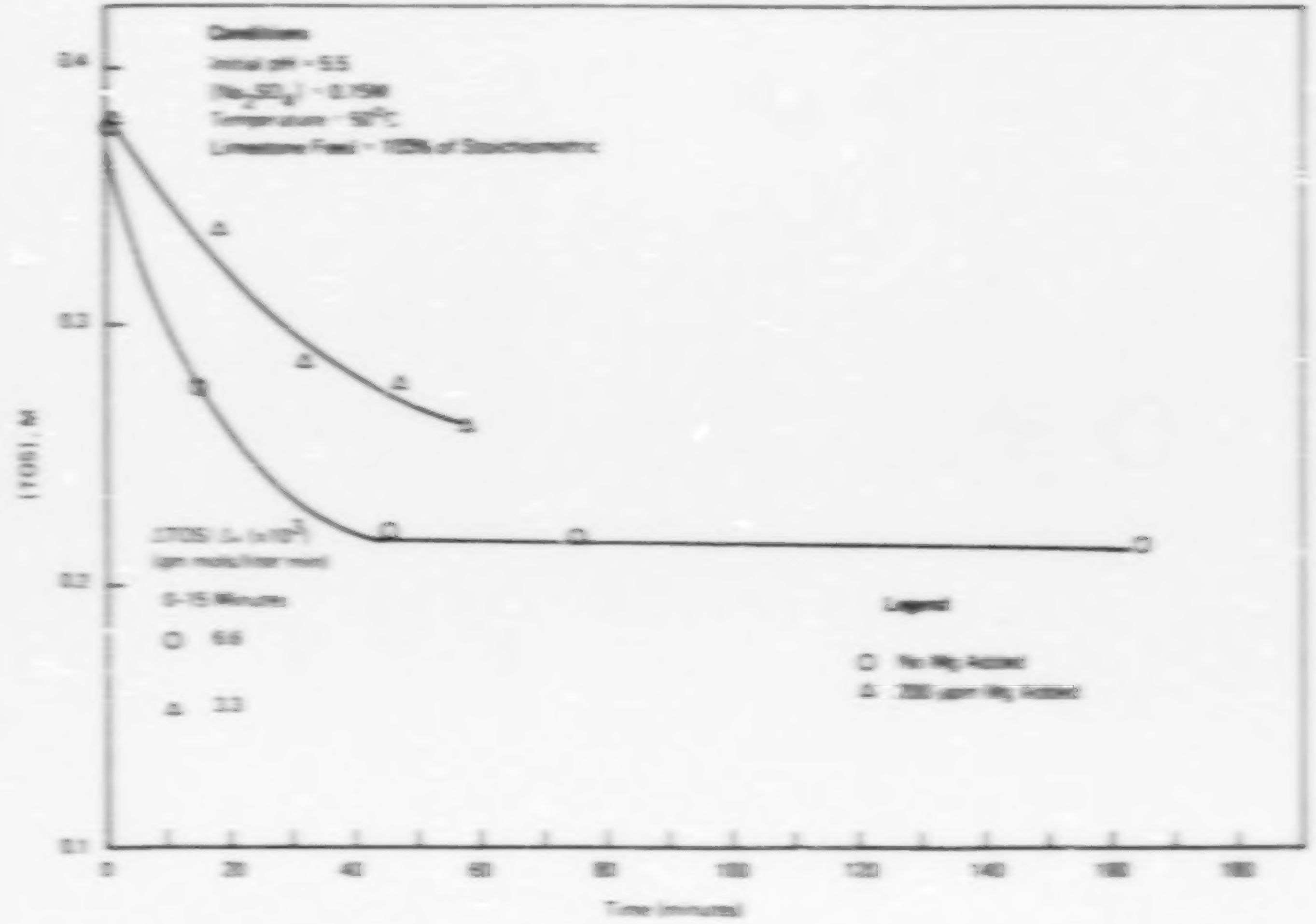


FIGURE VI-8 EFFECT OF SOLUBLE MAGNESIUM ON BATCH REGENERATION REACTION RATES WITH FREDONIA LIMESTONE

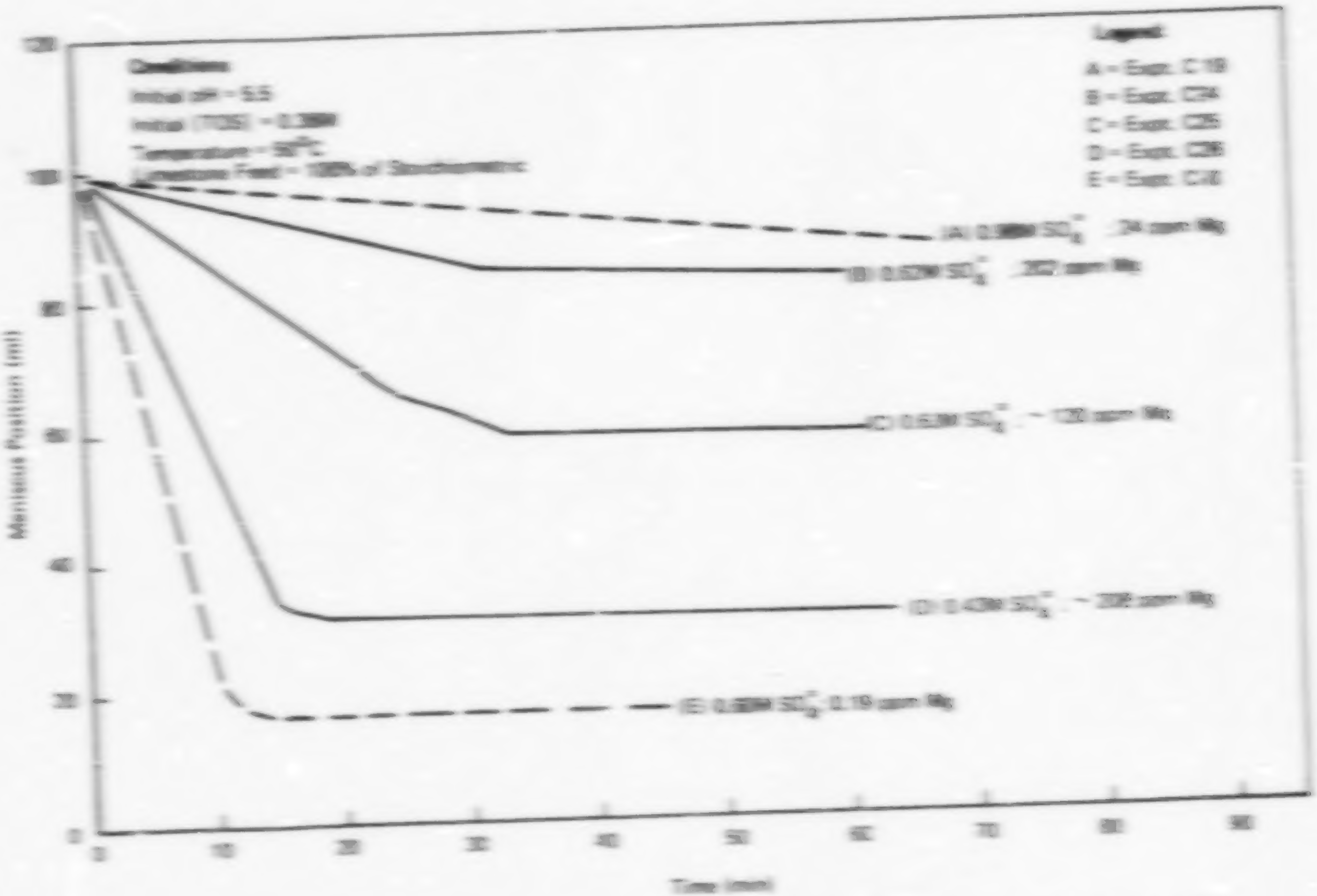


FIGURE VI-6 SETTLING BEHAVIOR OBSERVED FOR SOLIDS PRODUCED IN A 30-MINUTE CSTR USING FREDONIA LIMESTONE

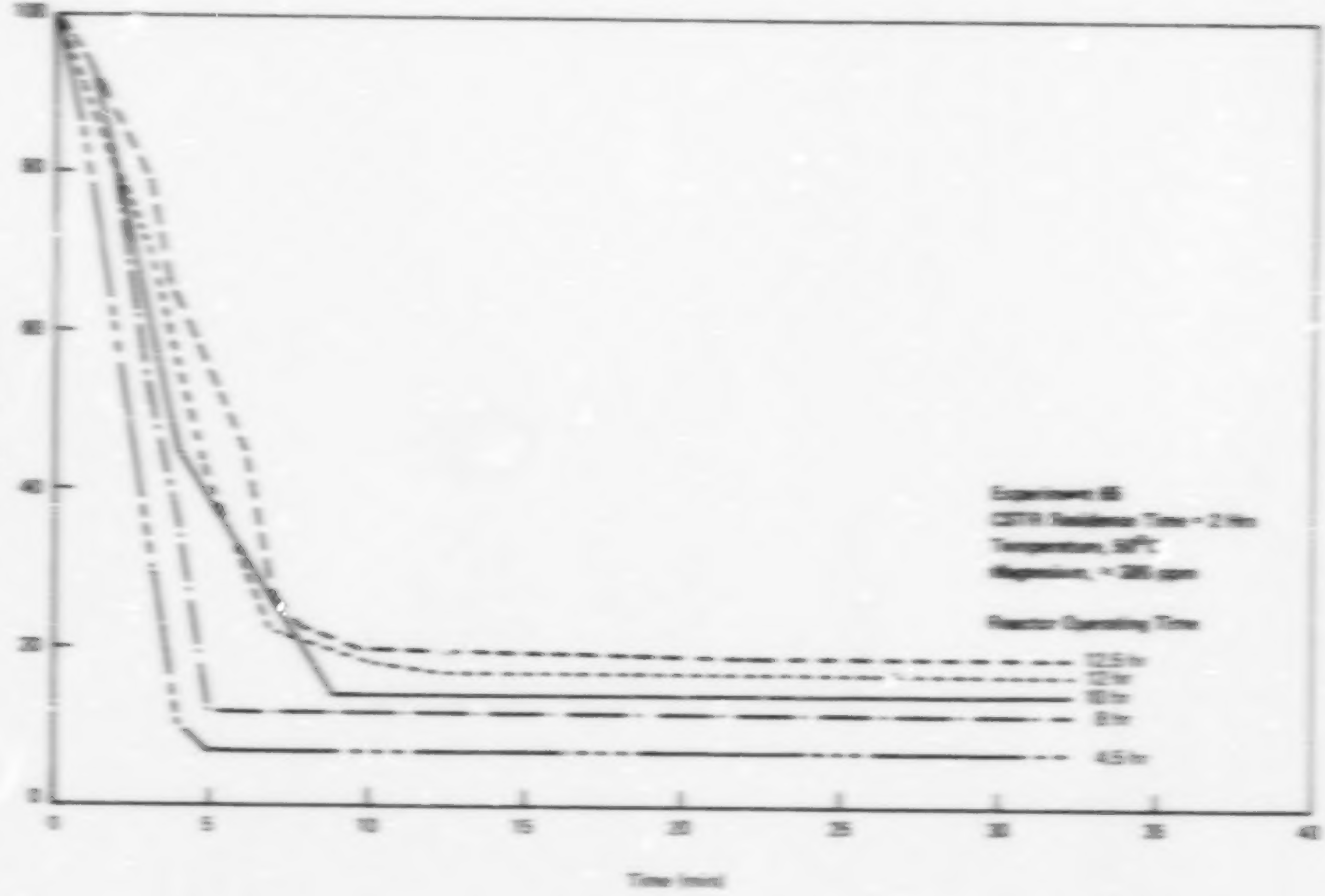


FIGURE VI–18 SETTLING BEHAVIOR OF SOLIDS PRODUCED DURING REGENERATION WITH LIMESTONE

reached in a closed-loop system producing a well washed filter cake. As shown in Figure VI-11, the solids did not settle as rapidly, nor did they compact as densely in experiment 66 as they had in the preceding experiment at 300 ppm magnesium. However, the solids still exhibited better settling properties than did those produced in the 50 minute CSTR with only 200 ppm of magnesium present.

In both of the 120 minute CSTR experiments, the settling properties seemed to deteriorate slowly as the experiment was allowed to continue. Plots of the final settled volumes observed at various times for both magnesium levels are shown in Figure VI-12. After 12 hours of reactor operation, the final settled volume appeared to be stabilizing in the higher Mg run (experiment 66) while it was still increasing steadily in the lower Mg run (experiment 65).

In an effort to improve solids characteristics at 2,200 ppm of Mg, three additional CSTR experiments were carried out with a different, single parameter changed in each. In experiment 67 the temperature was increased from 50°C to 80°C; in experiment 68 a two-stage ADL reactor (a 15 minute CSTR followed by a 120 minute CSTR) was substituted for the single CSTR; and in experiment 69 effluent solids were recycled to increase the suspended solids in the reactor from 2% to 6%.

Analyses of the effluent liquors from experiments 65 through 69 are shown in Table VI-1. Based on the drops in TOS and acidity across the reactor, increasing the magnesium level from 300 ppm to 2,200 ppm resulted in about a 10% decrease in the extent of the regeneration reaction. Each of the three changes in operating conditions at 2,200 ppm Mg increased the extent of reaction. As compared to experiment 66, the improvement in TOS reduction across the reactor was about 14% with the ADL reactor and the CSTR with solids recycled, and about 6% for the CSTR operated at 80°C.

Analyses of the properties of the solids produced in the five experiments are shown in Table VI-2. On the basis of the solids analysis, the increased magnesium level in experiment 65 resulted in a reduction in utilization of about 12%. In both experiments 65 and 66, exhaustive vacuum filtration of the product slurry on a laboratory Buchner funnel produced a filter cake containing only slightly more than 32% solids.

Utilizations in experiments 67-69 were consistently greater than those observed in experiment 66 which was also run at 2,200 ppm magnesium. While all the product slurries filtered rapidly, there were differences in the moisture contents of the filter cakes. Relative to the solids from experiments 65 and 66, using the ADL reactor or solids recycle improved filtration somewhat, but the solids from the 80°C run (experiment 67) could be dewatered best of all.

Settling curves for experiments 65-69 are illustrated in Figure VI-13. It can be readily observed that the three different changes in operating

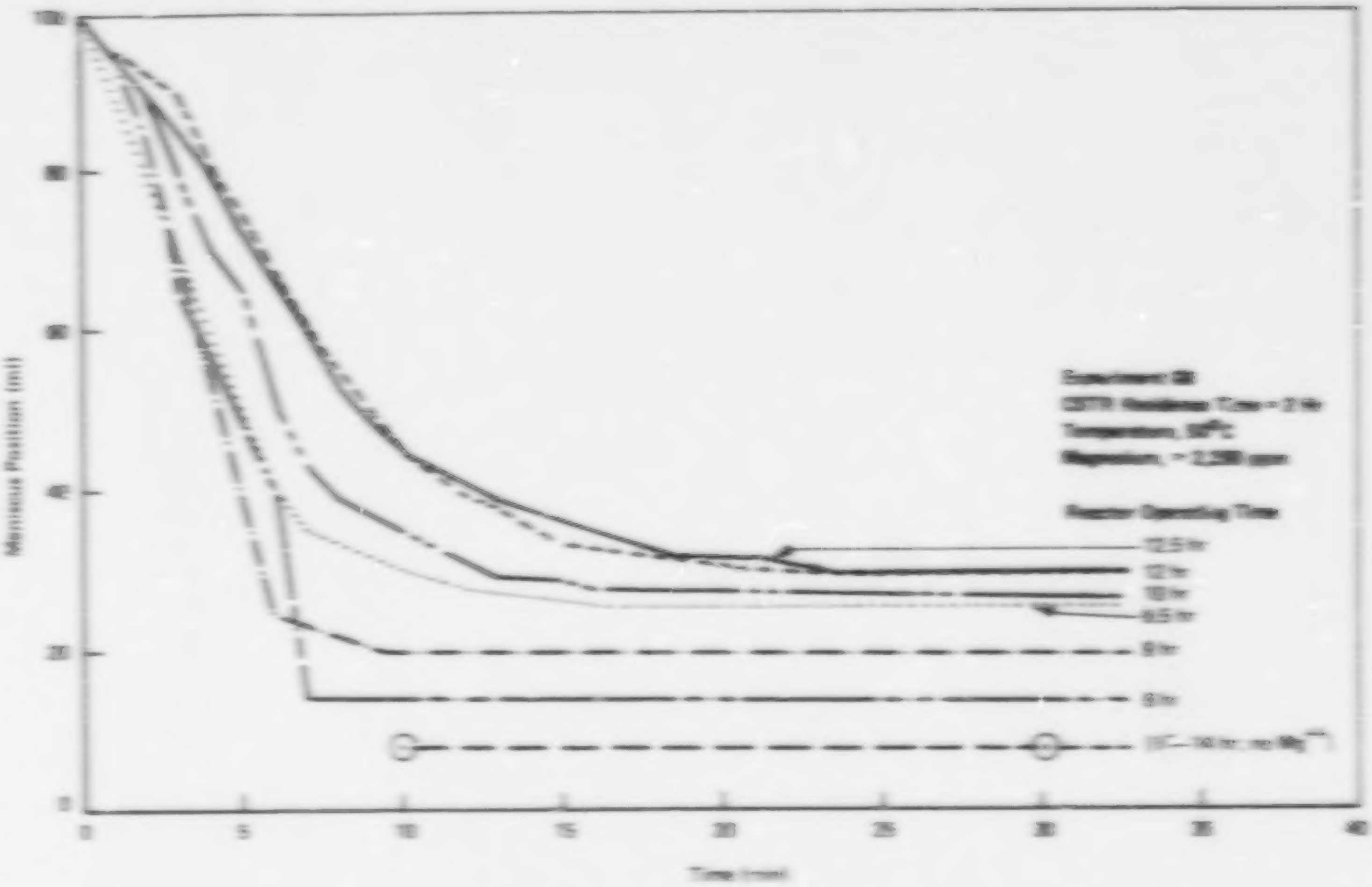


FIGURE VI-11 SETTLING BEHAVIOR OF SOLIDS PRODUCED DURING REGENERATION WITH LIMESTONE

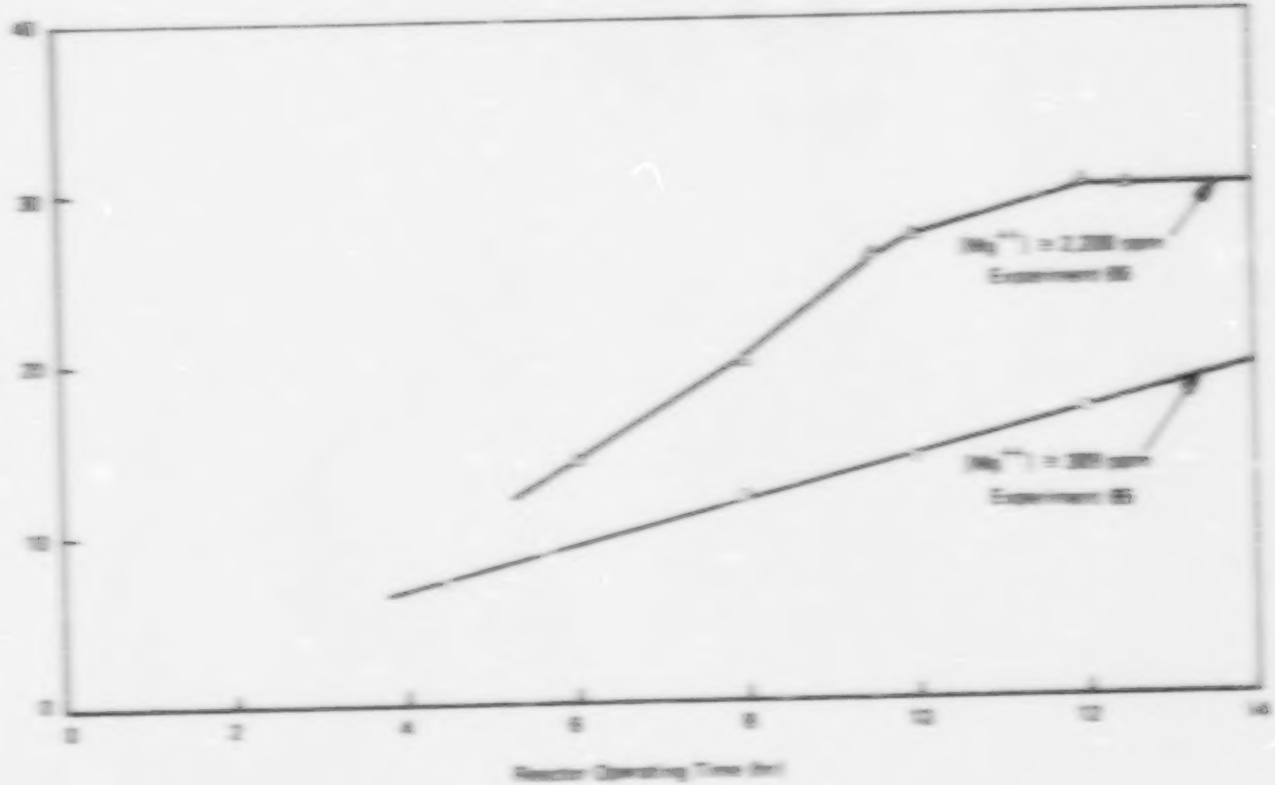


FIGURE VI-12 CHANGE IN SETTLED VOLUME OF EFFLUENT SLURRY SOLIDS AS A FUNCTION OF REACTOR OPERATING TIME – EXPERIMENTS 65 AND 66

TABLE VI-1

Solution Compositions Observed During Regeneration with Limestone in Continuous Reactors[a]

Expt.	Exp'l. Conditions	Stream	$SO_3^{=}$, M	[illegible], M	$SO_4^{=}$, M	pH	[illegible], M	Ca^{++}, M	[illegible], M
41	Lower Temperature, 30°C	Feed	.0179	.365	.336	5.37	7.62	0	0
	(CSTR, τ = 2 hr, 300 ppm Mg^{++})	Effluent	.0147	.251	.334	6.55	1.84	0.0036	0.12
44	Baseline Expt., 50°C	Feed	.0485	.350	.324	5.32	0.63	0	0
	(CSTR, τ = 2 hr, 2,200 ppm Mg^{++})	Effluent	.0394	.251	.132	6.40	0.61	0.0047	0.129
47	Higher Temperature, 90°C	Feed	.0463	.357	.324	5.25	0.60	0	0
	(CSTR, τ = 2 hr, 2,200 ppm Mg^{++})	Effluent	.0451	.317	.129	6.54	0.64	0.0023	0.125
49	All Reactors, 50°C τ = [illegible] = 2 hours, 2,200 ppm Mg^{++}	Feed	.0463	.342	.328	5.31	0.60	0	0
		Effluent	.0465	.327	.088	6.04	0.65	0.0037	0.125
44	Solids Recycle [illegible], 50°C	Feed	.0364	.336	.304	5.30	0.90	0	0
	(CSTR, τ = 2 hr, 2,200 ppm Mg^{++})	Effluent	.0413	.335	.334	6.70	—	0.0036	—

[a] Limestone (Fredonia) fed at 100% stoichiometry (the exact amount required to neutralize HSO_3^- fed).

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TABLE VI-2

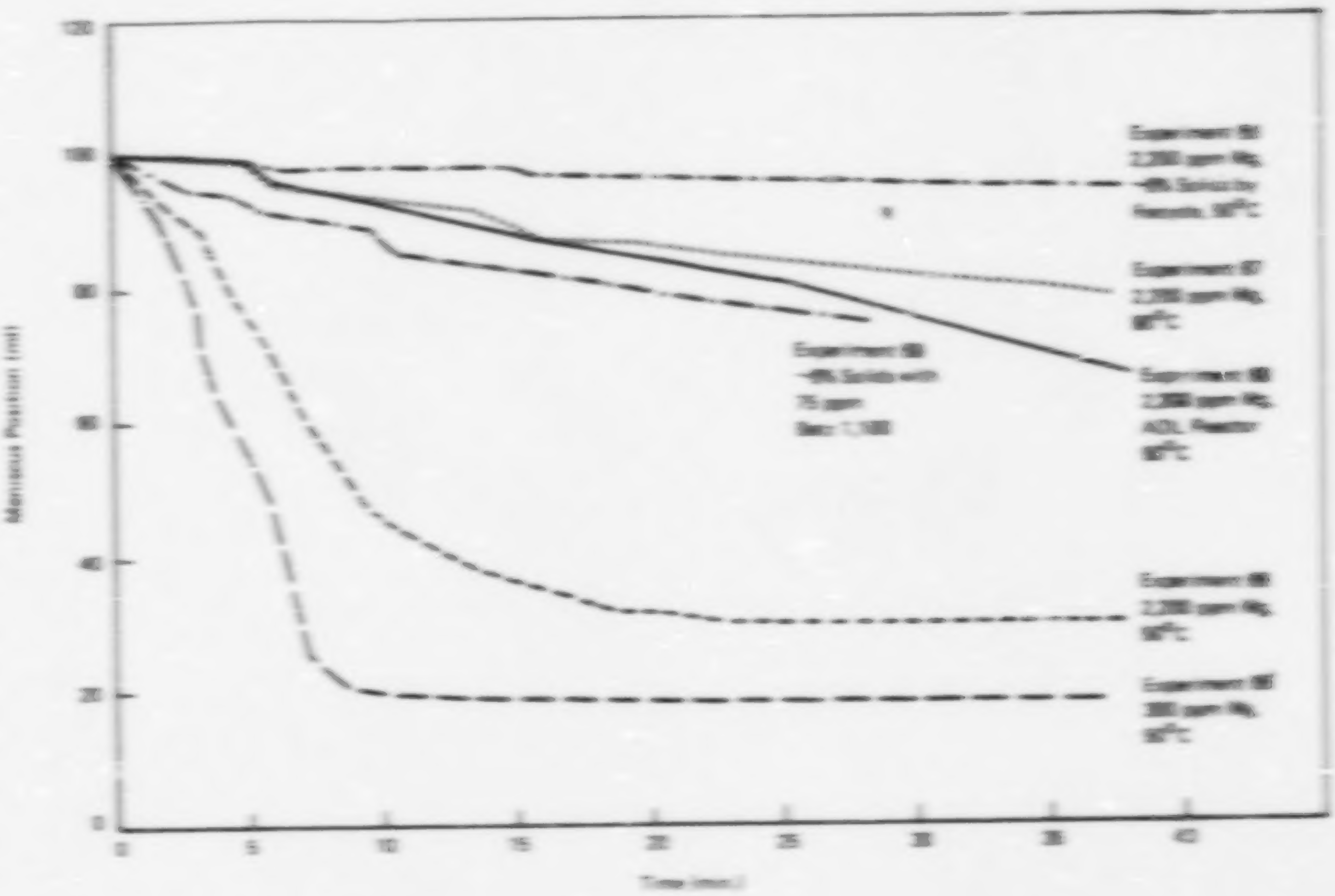
COMPOSITIONS AND CHARACTERISTICS OF SOLIDS PRODUCED DURING REGENERATION WITH LIMESTONE

Expt.	Experimental Conditions	Species in Solids (mm/g)					% $CaSO_4$/$CaSO_3$ [b]	% Utilization [c]	% Solids in wet cake [c]
		Ca^{++}	Mg^{++} [a]	TOS	$SO_4^=$	$CO_3^=$			
65	Lower Magnesium, 50°C CSTR, τ = 2 hours, 350 ppm Mg^{++}	7.49	0.09	5.78	0.63	2.01	9	77	33
66	Baseline Expt., 50°C CSTR, τ = 2 hours, 2,200 ppm Mg^{++}	7.86	0.14	4.89	0.54	2.62	8	65	32
67	Higher Temperature, 80°C CSTR, τ = 2 hours, 2,200 ppm Mg^{++}	7.90	0.18	5.76	0.48	—	7	74	47
68	426 Reactor, 50°C τ = 2 hours, 2,200 ppm Mg^{++}	7.84	0.14	5.28	0.76	2.28	12	76	40
69	Solids Recycle (? 6 wt. %), 50°C CSTR, τ = 2 hours, 2,200 ppm Mg^{++}	7.77	0.13	5.17	0.76	—	8	72	43

[a] Magnesium analyses by atomic absorption; Fredonia limestone contained 0.17 mmMg/g.

[b] Corrected for sodium sulfate physically trapped; magnesium sulfite and sulfate not included in ratio.

[c] ~2% total suspended solids, except for the recycle case.



Note: All settling samples taken after 12 hours of reactor operation.
Both CSTR and ADL Reactors had 2-hour residence time.

FIGURE VI-13 SETTLING BEHAVIOR OF SOLIDS PRODUCED DURING REGENERATION WITH LIMESTONE IN CONTINUOUS REACTORS

conditions all resulted in slower initial settling rates and increased final settling volumes. Of the curves presented, the ADL reactor solids and solids from experiment 69, after treatment with a flocculant, Betz 1100, appeared to have the best settling properties. However, neither material settled as well as that from experiments 65 and 66.

3. Studies of Liming for Magnesium Control and the Use of Flocculants to Improve Dewatering Properties

Experiments 65-69 indicated that regeneration with limestone could be carried out successfully in the presence of soluble magnesium ranging from 300 ppm to 2,200 ppm in a continuous stirred tank reactor (CSTR) with a residence time of about two hours. Because of the decreased limestone utilization and, more importantly, the degradation in solids settling and filtering properties at the higher magnesium level, it was concluded that some means of magnesium control and/or the use of flocculating agents to improve settling ought to be investigated for inclusion in a viable limestone-based dual alkali process.

Initial studies of the use of lime to control soluble magnesium were conducted in conjunction with experiments 65 and 66. Several times throughout the course of each experiment, 300 g to 500 g samples of the effluent slurry were collected, placed in beakers, stirred, and the pH monitored as known amounts of lime were added. At each of several pH values the slurry was allowed to react for 5-10 minutes. Liquor samples were then removed and the supernatant liquors later analyzed for soluble magnesium. Data on pH, amount of lime added, and final dissolved magnesium concentration are shown in Table VI-3 for effluents from the CSTR experiments which contained 300 ppm and 2,200 ppm of soluble Mg^{++}. The results for the two 300 ppm cases show that much of the Mg^{++} could be precipitated by adding lime to a pH of 10.6. Small increments of lime above that level (to pH ~ 11.3) removed essentially all remaining magnesium. Since the initial magnesium level was low (0.014M), a large portion of the total lime (about 0.1 mol/l of solution) was used for precipitating sulfite.

The data for the two 2,200 ppm tests affirmed the previous results. Although only 0.09-0.096 mol of lime per liter of solution should have been required to remove all of the Mg^{++}, 0.18-0.19 mol of lime was actually used. The excess lime was again about 0.09M and was used for removal of sulfite. On the final 2,200 ppm post-liming test, TOS measurements were made and, assuming $HSO_3^-/SO_3^=$ = 9:1, the decrease in TOS agreed with the amount of excess lime needed. It should be noted that at the measured solution carbonate levels of 0.02-0.03M, very little lime was consumed in forming calcium carbonate.

To study these options more carefully, CSTR experiments at 50°C and two hours of residence with soluble magnesium levels of 2,200 ppm and 300 ppm, which were duplicates of earlier experiments, were performed. The ability of a flocculating agent to improve the solids settling properties of the limestone reaction product slurry was studied.

TABLE VI-3

MAGNESIUM CONTROL BY LIMING CSTR PRODUCT SLURRY

Sample[a]	pH	Soluble Mg^{++} (Mols/l of Solution)	$Ca(OH)_2$ Added (Mols/l of Solution)
≈300 ppm Mg^{++}, (4τ)	6.35	0.0140	0.000
	10.6	0.0038	0.100
	11.2	0.0009	0.103
	11.6	0.0003	0.105
≈300 ppm Mg^{++},(5τ)	6.5	0.0145	0.000
	10.5	0.0066	0.0847
	11.3	0.0000	0.0942
	11.6	0.0000	0.0970
≈2,200 ppm Mg^{++}, (5τ)	6.6	0.0896	0.000
	11.6	0.0000	0.191
	11.9	0.0000	0.196
≈2,200 ppm Mg^{++}, (5τ)	6.6	0.0958	0.000[b]
	10.0	0.0165	0.181[c]
	11.6	0.0008	0.206

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[a] Slurry sample taken after reactor operated for the indicated number of residence times, τ.

[b] [TOS] = 0.262

[c] [TOS] = 0.070

A second CSTR with a residence time of 30 minutes was placed after the limestone reactor to verify the results of earlier batch studies in which lime was used to control soluble magnesium levels. In these studies, we attempted to reproduce as closely as possible the conditions employed in experiment 66 (2,200 ppm magnesium) and experiment 65 (300 ppm magnesium) discussed previously. Solution concentrations entering the reactor (after dilution by water accompanying the limestone slurry) were: $SO_4^=$, 0.6M; TOS, 0.15M; pH, 5.4; limestone feed stoichiometry, about 100%.

Regeneration in the presence of about 2,200 ppm magnesium was studied in experiment 70, and as is evident from Figure VI-14, the solids in the product slurry settled very poorly. This behavior was in marked contrast to that observed when the same experiment had been conducted earlier. The range of final settled volumes observed previously (experiment 66) is included in Figure VI-14 for reference. Adding a polyelectrolyte flocculating agent (Betz 1100) at concentrations ranging from 1 ppm to 20 ppm improved settling behavior to some extent, more or less in proportion to the concentration at which it was added (dotted curves in Figure VI-14). Figure VI-14 also shows that the solids in the final slurry after reaction with lime settled no better than those which had emerged from the limestone reactor.

The solids generated in experiment 71, in which 300 ppm of magnesium was present, also settled more poorly than did those generated in the corresponding earlier experiment (experiment 65) as shown in Figure VI-15. As in the earlier experiment, the final settled volume increased as the limestone CSTR was allowed to continue to operate. From an unsettled volume of 100 ml, the final settled volume increased from about 17 ml after six hours of operation to about 40 ml when the experiment was terminated after eleven hours. Weight percent solids in the slurry ranged from 1.7% to 1.8%. The effect of adding Betz 1100 flocculating agent at the 0.05 ppm level to the final slurry sample taken after eleven hours of operation is shown by the dashed line in Figure VI-15. While the final settled volume was not reduced markedly, the initial settling rate was significantly improved. By visual observation, addition of the flocculating agent seemed to be particularly effective in coagulating the finer particles which settled more slowly and were causing a persistent haze in the portion of the supernate from which most of the solids has already settled.

Figure VI-16 shows that after reacting the limestone regenerated product slurry with lime to remove magnesium, the initial settling rate of the combined solids from the final reactor was slower than that observed after the initial limestone reaction. The final settled volume, however, was improved by the liming reaction. Addition of 1 ppm of Betz 1100 again caused a marked change in the initial settling rate of the lime reactor solids. The final settled volume was essentially not changed by the addition of the agent.

A summary of the reactant solution concentrations employed in experiments 70 and 71 and the changes in amounts of soluble species in solution across each of the two reactors is shown in Table VI-4. Because both the limestone fed to the first reactor and the lime fed to the second were fed

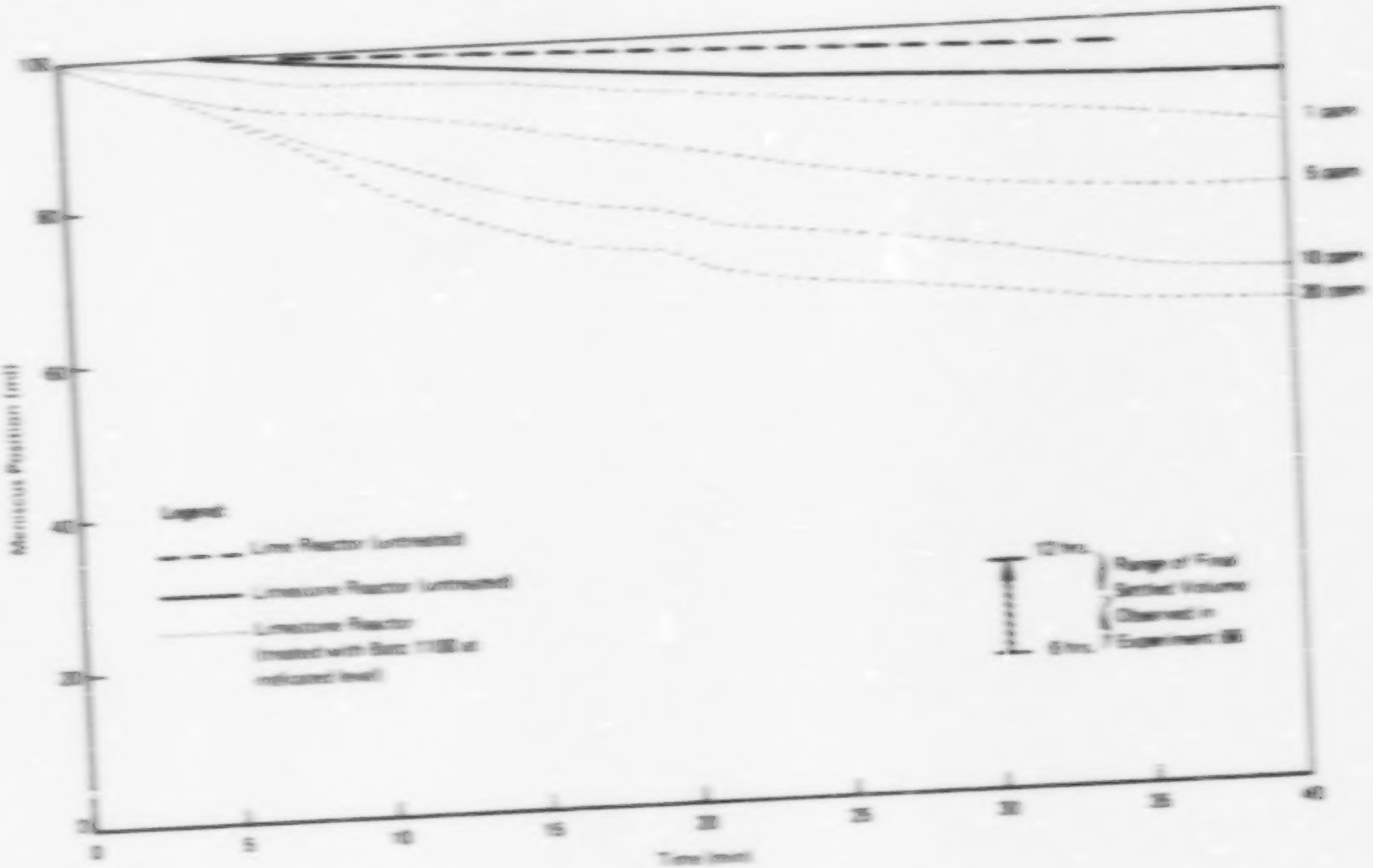

FIGURE VI-14 SETTLING BEHAVIOR OF SOLIDS PRODUCED IN THE PRESENCE OF 2,200 ppm MAGNESIUM – EXPERIMENT 70

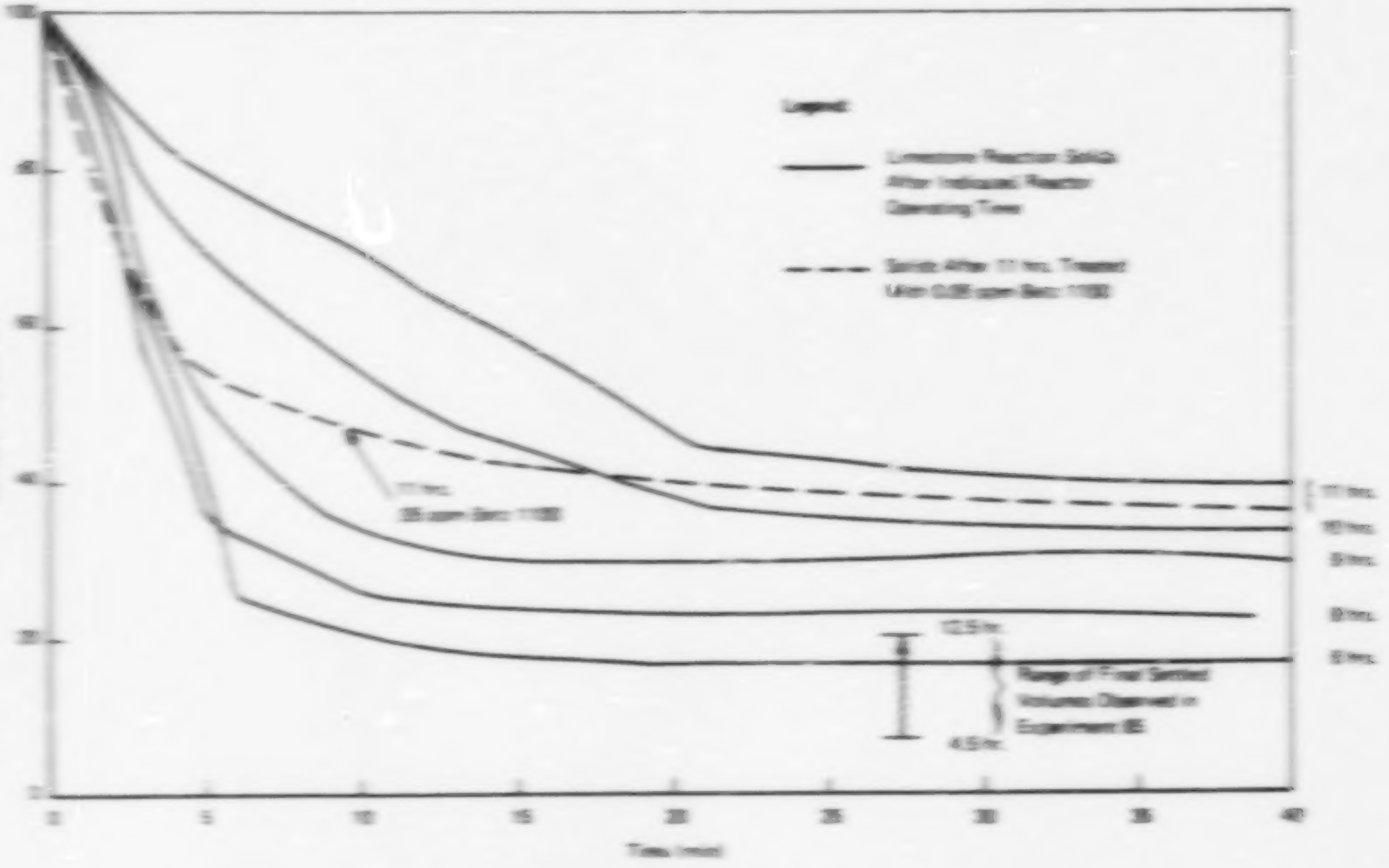

FIGURE 11–15 SETTLING BEHAVIOR OF SOLIDS PRODUCED DURING REGENERATION WITH LIMESTONE IN THE PRESENCE OF 300 ppm MAGNESIUM — EXPERIMENT 71

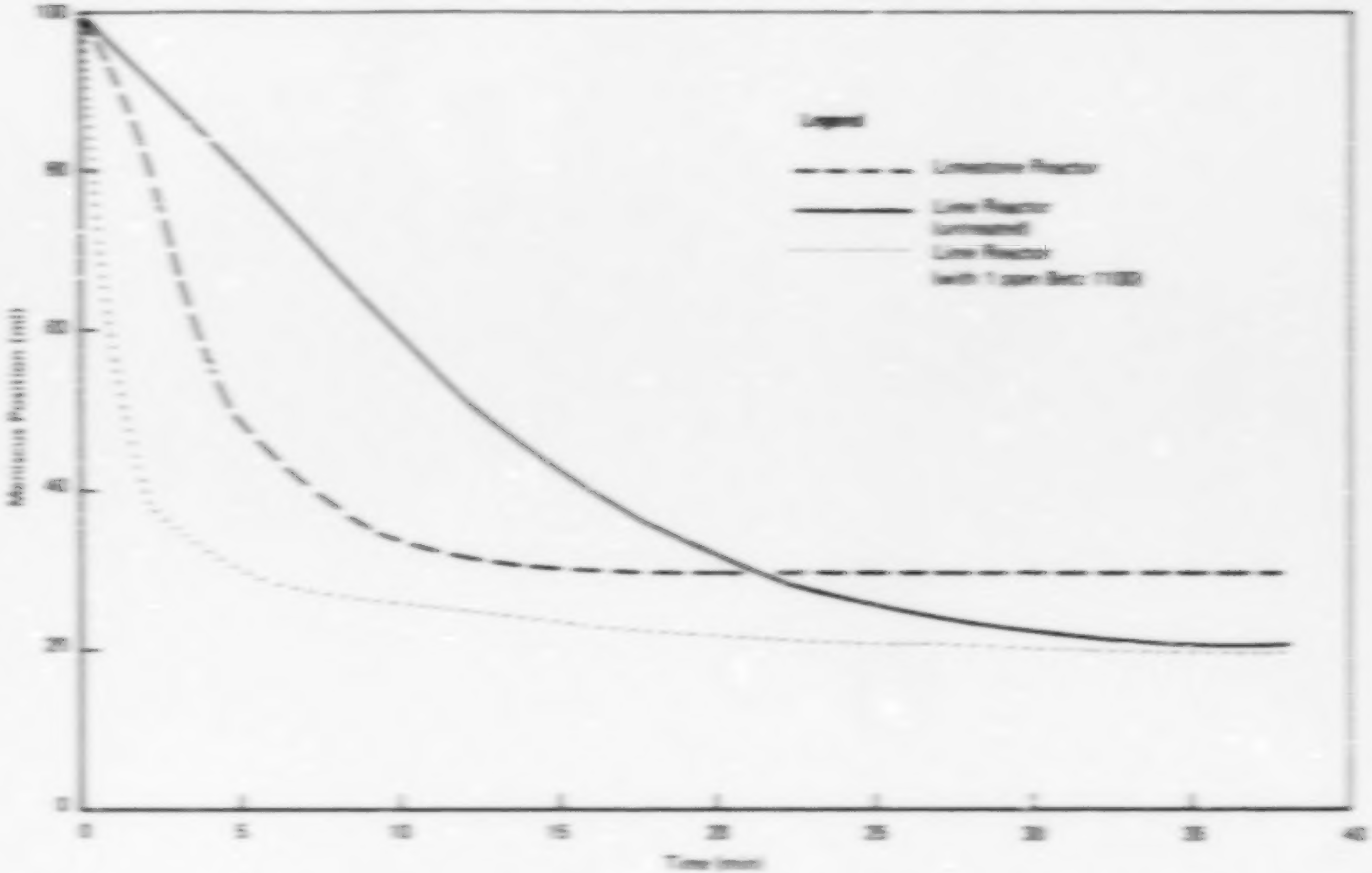

FIGURE VI-15 COMPARISON OF SETTLING BEHAVIOR OF SOLIDS PRODUCED DURING REGENERATION WITH LIMESTONE IN THE PRESENCE OF 300 ppm MAGNESIUM AFTER 5 HOURS OF REACTOR OPERATION

TABLE VI-6

LIMESTONE/LIME SERIES REACTOR PERFORMANCE[a]

Reactor Feed Concentrations (M)[b]	Expt. 71 (∿300 ppm Mg^{++})	Expt. 70 (∿2,200 ppm Mg^{++})
TOS	0.322	0.325
Acidity	0.287	0.296
$SO_4^=$	0.586	0.608
Mg^{++}	0.014	0.089
pH	5.4	5.4
Limestone (%)[c]	115	115
Change Across Limestone Reactor (mmols/min)		
TOS	-2.60	-2.05
Acidity	-4.93	-4.76
Mg^{++}	+0.01	-0.09
$CO_3^=$	+0.35	+0.44
Effluent pH	6.8	6.6
Change Across Lime Reactor (mmols/min)		
TOS	-1.7	-1.49
Acidity	-2.68	-1.39
Mg^{++}	-0.36	-2.15
Effluent Solution Concentrations (M)		
TOS	0.102	0.068
Ca^{++}	0.0026	0.005
$CO_3^=$	0.0082	0.006
Mg^{++}	0.0002	0.0009
pH	11.75	11.95

[a] Initial limestone reactor, 2 hour CSTR; lime reactor 0.5 hour CSTR.

[b] After dilution by water in limestone slurry fed.

[c] % of stoichiometric amount equivalent to bisulfite fed.

as slurries, account needed to be taken for the diluting effect of the slurry water. To make them more understandable, the changes in concentrations in each of the two reactors are expressed as fluxes in units of mmols/min. In experiment 71, in which about 300 ppm of magnesium was removed during the lime reaction, about 60% of the total TOS removed by the combined reactors in series occurred during the reaction with limestone. In experiment 70, where a significantly greater amount of magnesium was removed, only about 40% of the total TOS which was precipitated occurred in the limestone reactor.

The reaction taking place in the lime reactor was essentially composed of two steps. The acidity remaining in solution after the limestone reaction was first neutralized -- for every two equivalents of acidity neutralized, one mol of calcium sulfite was precipitated.

$$Ca(OH)_2(s) + 2HSO_3^- \rightarrow CaSO_3(s) + SO_3^= + H_2O \qquad (27)$$

After neutralization was completed, the hydroxide produced from the continued dissolution of lime reacted with magnesium to precipitate magnesium hydroxide.

$$Ca(OH)_2(s) + Mg^{++} + SO_3^= \rightarrow Mg(OH)_2(s) + CaSO_3(s) \qquad (28)$$

The calcium ion produced reacted with sulfite to precipitate additional calcium sulfite. The amount of TOS removed during neutralization remained relatively constant regardless of the amount of magnesium present, while the TOS removal accompanying magnesium hydroxide precipitation was directly proportional to the amount of magnesium removed. Thus, the 2.68 mmols/min reduction in acidity observed in experiment 71 (Table VI-4) was accompanied by the removal of 1.34 mmols/min of TOS from solution. The remaining TOS which was removed during the lime reaction was essentially equal to the 0.36 mmols/min of magnesium removed.

The characteristics of the solids produced in the initial limestone reactor and the combined solids after treatment with lime in the second reactor are shown in Table VI-5. The 78% utilization observed in experiment 71 was quite similar to utilizations observed previously in two hour CSTR experiments at low magnesium levels. The decrease in utilization to 68% at the higher magnesium level reflects the inhibition of the regeneration reaction which was also observed previously.

The amounts of magnesium in the well-washed limestone reactor solids increased as the soluble magnesium concentration increased. The magnesium remaining in the solids is a significant fraction of the magnesium present in the limestone reagent. The Fredonia limestone used in these experiments had a magnesium content of 0.017 mmols of magnesium per mmol of calcium. The Mg/Ca mol ratio in the solids from experiment 71 was 0.012. Thus,

TABLE VI-5

LIMESTONE/LIME SERIES REACTOR SOLIDS PROPERTIES

Species in Limestone Reactor Solids (mmole/g)	Expt. 71 ($\sim$300 ppm Mg^{++})	Expt. 70 ($\sim$2,200 ppm Mg^{++})
Ca^{++}	7.70	7.85
Mg^{++}	0.09	0.14
TOS	5.60	4.94
$SO_4^=$	0.49	0.62
$CO_3^=$	1.80	2.38
$(CaSO_4)/(CaSO_x)$	7%	7%
Limestone Utilization	78%	68%
Wet Cake Solids	34%	30%

Species in Combined (LS+Lime) Reactor Solids (mmole/g)	Expt. 71	Expt. 70
Ca^{++}	7.51	7.66
Mg^{++}	0.46	1.82
TOS	5.10	4.90
$SO_4^=$	0.43	0.52
$CO_3^=$	n.a.[a]	1.27
OH^-	1.30	2.45
$(CaSO_4)/(CaSO_x)$	7%	8%
Wet Cake Solids	37%	38%

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[a] Not Analyzed.

with about 300 ppm of soluble magnesium in the reactor, approximately two-thirds of the magnesium which entered with the limestone remained in the solids. In experiment 70, the Mg/Ca mol ratio can be calculated to be 0.018; with 2,200 ppm of magnesium in the reacting solution, some of the soluble magnesium was actually being purged in the limestone cake.

Analyses of the solids from the two-reactor sequence indicated that the $CaSO_3/CaSO_4$ ratio of about 7% was maintained during the lime treatment. The amount of hydroxide in the final combined reactor solids does not represent unutilized lime, but, rather, the solid magnesium hydroxide present. In fact, in both experiments, the amounts of hydroxide found were lower than would be expected for the amounts of magnesium precipitated. The low hydroxide results are caused by the insolubility of magnesium hydroxide and resulting difficulties in completely titrating it.

C. PILOT PLANT OPERATIONS

As in the evaluation of the concentrated active sodium mode using lime for absorbent regeneration, pilot plant testing in the concentrated limestone mode was focused on the performance of the regeneration system. Of primary concern was the determination of the effects of principal reactor operating and design parameters (i.e., operating pH, reactor configuration, and reactor holdup time) and system variables (i.e., sulfate concentration or sulfate-to-active-sodium ratio and type of limestone) on reactor performance. The purpose was to develop a viable reactor design and establish the range of operating conditions that would ensure better than 80% utilization of limestone and waste solids that could be filtered to a minimum of 45% insolubles.

Preliminary open-loop runs in the pilot plant confirmed laboratory results regarding the difficulties associated with implementing a limestone dual alkali system. Three runs made using a single CSTR and a natural calcite (Marblewhite 200 obtained from Pfizer) with a feed liquor comparable to that in a concentrated-lime mode operation (containing no soluble magnesium) showed very low limestone utilization and generally poor solids settling properties. Table VI-6 summarizes the general conditions and results of these three runs. Even operating with a reactor holdup time of two hours or increasing the calcite feed rate to more than twice that required to neutralize all the acidity present in the feed liquor, the pH in the effluent from the reactor could not be increased above 6.05.

Based upon these unfavorable results and the extensive laboratory testing, it was decided to utilize a multistage reactor system in subsequent pilot plant operations. Such a system would approach plug flow or batch reactor performance and would allow close monitoring of the reactor performance as the reaction proceeds. The best performance obtained in laboratory studies had been in batch reactor studies; the multistage approach to the plug flow reactor should produce similar results as the batch reactor but in continuous operation. Fredonia limestone was also used rather than Marblewhite 200 in all subsequent runs, as laboratory testing had shown Fredonia limestone to be the more reactive.

TABLE VI-4

SUMMARY OF PRELIMINARY OPEN-LOOP RUNS USING A SINGLE CSTR WITH MARBLEHEAD LIMESTONE

Feed Liquor: pH = 3.8
[TOS] = 0.48M
[$SO_4^=$] = 0.65M
[Mg^{++}] = 0
[Ca^{++}] = 0
[CO_2] = 0
Temp. = 48-52°C

Reactor Conditions			Effluent Liquor			Performance			
							Sulfate	Settling	
Holdup (hrs.)	Solids Recycle	Limestone Feed (% to Neutralize HSO_3^-)	pH	[TOS] (M)	[Ca^{++}] (ppm)	Limestone Utilization	Precipitation mole $CaSO_4$ / mol $CaSO_x$	Time (mins.)	Final Volume (ml)[c]
1	No	115	5.9	0.41	210	10-15%	.25	8	78
2	No	135	6.0	0.39	190	15-20%	.22	10	125
3	to ~10%[a]	215	6.0	—	440	<20%[b]	.34	~60	~500

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[a] Using washed filter cake from previous runs with lime

[b] Estimated based upon analyses of product solids and recycled filter cake used.

[c] 1,000 ml graduate used for pilot plant settling tests.

1. Open-Loop Multistage Testing

A total of nine runs was made using a reactor system consisting of six CSTR's arranged in series. The six reactors were identical in design. Each was a polyethylene tank fitted with four baffles, and a center entering propeller-type stirrer. The six tanks were arranged for gravity liquor flow with discharge baffles around the overflow ports to ensure no short-circuiting of the feed liquor. Slurry from the last reactor was sent directly to the pilot plant rotary drum vacuum filter for solids dewatering. It was hoped that the filter operation would help to characterize the solids properties.

Table VI-7 lists the basic test conditions and the range of variables explored. In all runs the composition of the reactor feed liquor used was made to simulate that anticipated for a system operating in a concentrated active sodium mode under closed-loop conditions.

Run 125 is considered to be the base case. It is a repetition of run 122 (not included in Table VI-7) in which an agitator failure led to questionable results. In the other seven runs the effects of four process variables on limestone utilization and solids properties were studied: sulfate (0.65M to 0.9M) and magnesium (25-2,250 ppm) concentrations in the simulated scrubber bleed; limestone feed stoichiometry (68-184%); and solids holdup time (by increasing reactor residence time or recycling product solids). In one run the liquor from the last (sixth) reactor was fed to another reactor where it was treated with lime to increase pH and precipitate magnesium (post-liming mode). Throughout all of the runs the temperature of the feed liquor was set at 52 ± 4°C (125 ± 7°F).

All runs were started with the reactors empty. Liquor and limestone feed to the first reactor were started simultaneously. The reactor liquors were then monitored with time to ensure that steady-state operation was achieved. Most of the runs lasted about five mean holdup times, a sufficient duration to closely approach steady-state liquor conditions.

Specific operating conditions for each run and the principal results are summarized in Table VI-8. Four process criteria have been used to characterize the reactor system operation and performance: calcium utilization; levels of soluble calcium and magnesium in the reactor effluent liquor; sulfate precipitation; and dewatering properties of the waste solids produced. These are discussed in the following subsections.

Reaction Rate and Limestone Utilization

Over the range of process conditions, limestone utilization varied from 20% to approximately 90-95% (based upon the average of the solids and liquid analyses). The effects of variations in process conditions confirmed the results of the laboratory program. In general, limestone utilization increased with increasing solids residence time. The highest utilization was achieved in run 127 in which product solids filtered from the last reactor liquor were recycled to the first reactor. Figure VI-17

TABLE VI-7

CONDITIONS FOR OPEN-LOOP MULTISTAGE REACTOR RUNS

Operating Conditions:

Feed Liquor	Run 125 Base	Range
pH	5.5 ± 0.2	-
[TOS], (M)	0.34 ± 0.02	-
$[SO_4^=]$, (M)	0.7 ± 0.05	0.65 - 0.9
$[Mg^{++}]$, (ppm)	350 ± 65	25 - 2,250
$[Ca^{++}]$, (ppm)	80 ± 20	-
$[CO_2]$, (M)	0.02 ± 0.01	-
Temp., (°C)	52 ± 4	-
Limestone Feed Stoichiometry, (%)[a]	85 ± 5	68 - 186

Runs Summary:

Run No.	Variable
120	High $CaCO_3$ stoichiometry
121	High magnesium
122	Base run
123	High sulfate
124	High sulfate and post-liming
125	Base run (repeat of 122)
126	Low $CaCO_3$ stoichiometry
127	Solids recycle
128	Extended reactor holdup time

[a] Calculated as available $CaCO_3$ feed/2 x HSO_3^- feed.

TABLE VI-9

SUMMARY OF OPEN-LOOP LIMESTONE RUNS IN MULTISTAGE REACTOR SYSTEM (FREDONIA LIMESTONE)

Feed Liquor: pH = 5.3-5.6
[TSO₂] = 0.32-0.38M
[Mg⁺⁺] = 60-150 ppm
[SO₄⁼] = 0.02M
Temp. = 49-50°C
Reactor Conditions: Temp. = 45-48°C
[illegible] = 1.2-22 (except Runs 128 & 127)

Run No.	Run Variable	Reactor Configuration No. of RSTR's x Min.	Solids Recycle	Liquid Feed [SO₂] (M)	Liquid Feed [Mg⁺⁺] (ppm)	Limestone Feed^b % to Neutralize Total [SO₂]	Effluent Liquid [TSO₂] (M)	Effluent Liquid [Oxidized] (M)	Effluent Liquid pH	Limestone Utilization Based on Solids Analyses	Limestone Utilization Based on Liquid Balance	mole CaSO₃/mole CaCO₃	Settling Time (min.)
121 to 122	BASE	4 x 15	No	0.35	425	92	0.238	0.242	6.2	74	75	0.73	8-10
123	High CaCO₃ Feed	4 x 15	No	0.40	290	200	0.260	0.060	6.45	—	56	—	12-14
124	Low CaCO₃ Feed	4 x 15	No	0.31	327	68	0.272	0.249	6.4	84	72	0.38	5-6
122	High Magnesium	4 x 15	No	0.4	1,230	74	0.294	0.267	5.7	24	24	0.34	23-27
125	High Sulfate	4 x 15	No	0.3	388	87	0.260	0.238	5.8	28	23	(0.23)	26-30
126	High Sulfate & Post Liming	4 x 15 + 1 x 30^a	No	0.39	25	80	0.249^c	0.207^c	6.0	44	37	0.28	12-16
127	Solids Recycle	4 x 15	Yes-40%^d	0.32	345	91	0.286	[illegible]	6.7	91	90	0.22	Very Poor
128	High Reactor Holdup	4 x 30	No	0.32	350	97	0.225	[illegible]	6.6	76	81	0.23	Poor (30-40)

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[a] Post liming was carried out in a separate reactor having 30 minutes residence time.

[b] Based on 93% available calcium carbonate in the raw limestone feed.

[c] Liquor from the post liming reactor had the following compositions: pH = 11
[TSO₂] = 0.249
[Mg⁺⁺] = [illegible]

[d] Solids recycled to first reactor were filtered solids from last reactor.

through VI-24 show the change in TOS concentration and acidity through the successive reactors in these eight runs.

The rate of reaction is also dependent on the availability of calcium from the limestone (or quantity of limestone present). The effect of calcium availability can be seen from the dependence of reaction rate on limestone feed stoichiometry in runs 120, 125, and 126. The average initial rate of reaction in these runs as determined from the decrease in TOS across the first reactor is plotted in Figure VI-25. As shown, the rate of reaction roughly doubled with almost a threefold increase in the limestone feed rate. This confirms similar laboratory results and indicates that limestone dissolution is one of the rate-limiting steps.

However, the mechanism and kinetics of calcium sulfite precipitation are important too. This is clear from the effects of solids recycle on the overall limestone utilization. Recycling product solids (which contained only about 10% unutilized calcium carbonate) increased utilization from about 75% in run 125 to over 90% in run 127. The increase in reaction rate is also apparent in Figures VI-17 and VI-23. It should be noted, though, that part of the difference in the initial TOS decrease between runs 125 (Figure VI-17) and 127 (Figure VI-23) is also partly due to the increase in limestone feed stoichiometry (82% in run 125 versus about 100% in run 127) and to the liquor occluded with the recycled solids. However, these factors account for only a small fraction of the overall difference in rates.

Soluble Calcium Concentrations

The rate of reaction is also reflected in the soluble calcium concentrations in the reactor system. Figures VI-26 through VI-29 show the concentrations of TOS and soluble calcium through successive reactors in the last four runs (calcium concentrations in the first four runs were measured only in the last reactor); and Figures VI-30 and VI-31 show soluble calcium concentration as a function of TOS in the first reactor (last four runs) and in the last reactor (all runs).

As shown, the soluble calcium concentration is related to the decrease in TOS (or increase in sulfite concentration by neutralization of bisulfite). Calcium levels increase to a high level in the first reactor where sulfite concentrations are low (but TOS high), and then decrease through the remaining reactors, tracking TOS (as sulfite concentrations increase).

It is not possible to correlate calcium concentrations directly with sulfite because sulfite is not measured directly and there are uncertainties in carbonate analyses and the bicarbonate/carbonic acid split that preclude accurate estimates of sulfite from TOS, acidity, and carbonate analyses. Since the estimates of sulfite concentration have some uncertainty, it is difficult to accurately determine the apparent solubility products ($[Ca^{++}] \times [SO_3^=]$) in these solutions. However, in

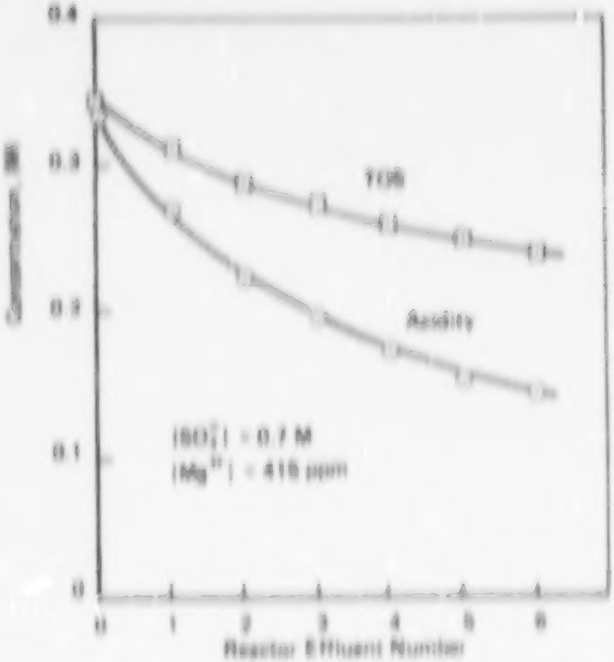


FIGURE VI-17 RUN 125 (BASE CASE)

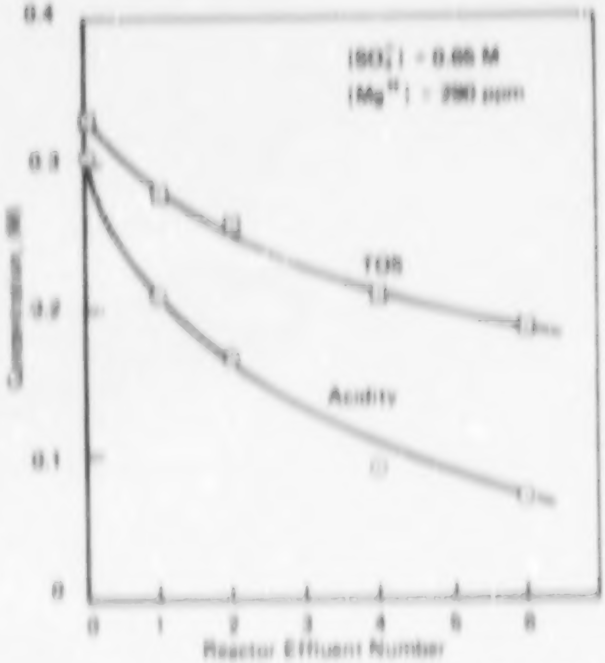


FIGURE VI-18 RUN 120 (HIGH CaCO$_3$ FEED)

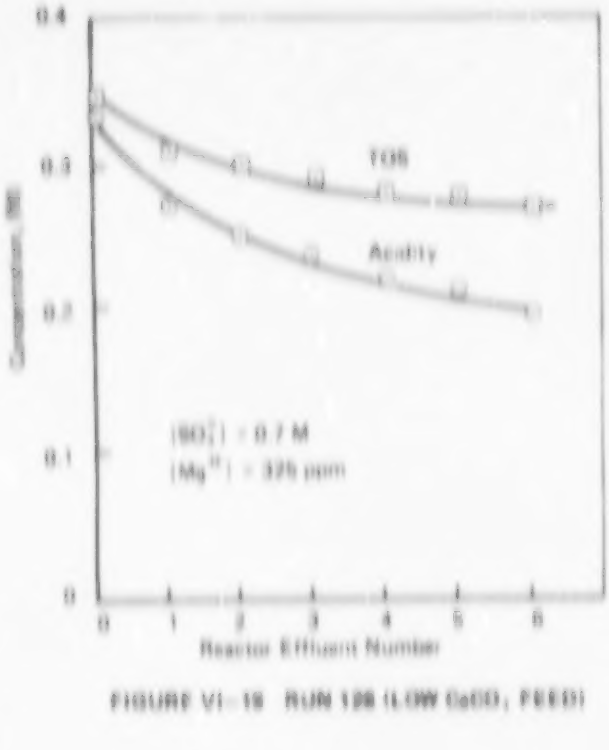


FIGURE VI-19 RUN 126 (LOW CaCO$_3$ FEED)

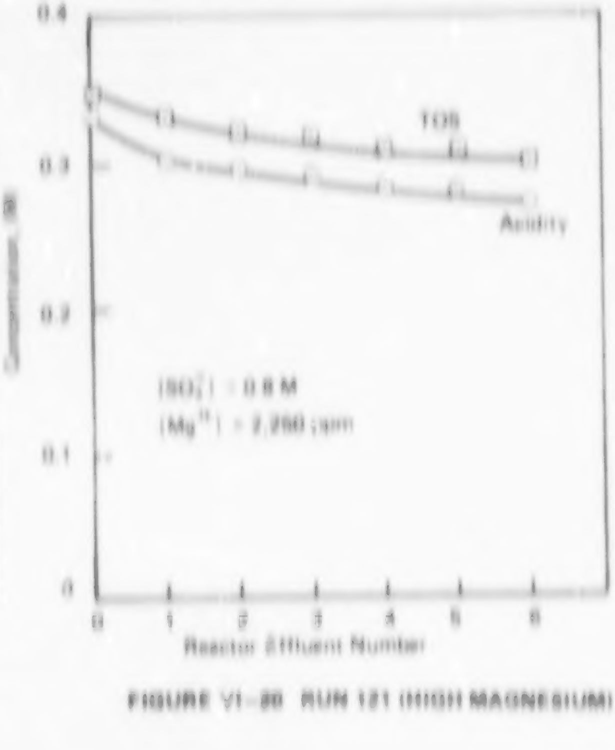


FIGURE VI-20 RUN 121 (HIGH MAGNESIUM)

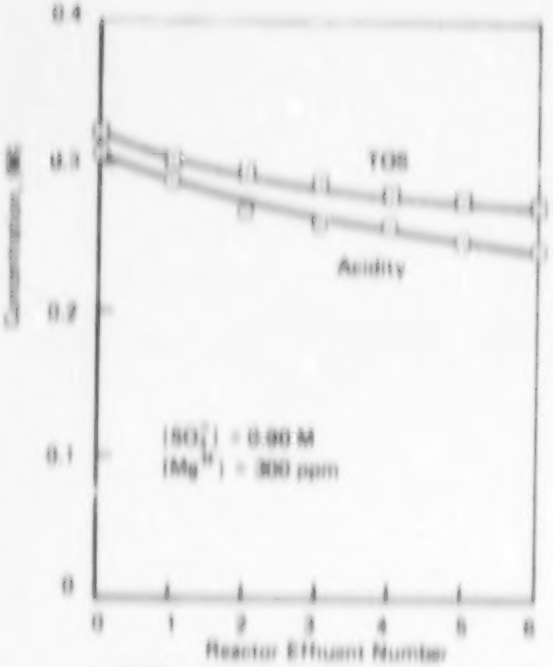


FIGURE VI-21 RUN 123 (HIGH SULFATE)

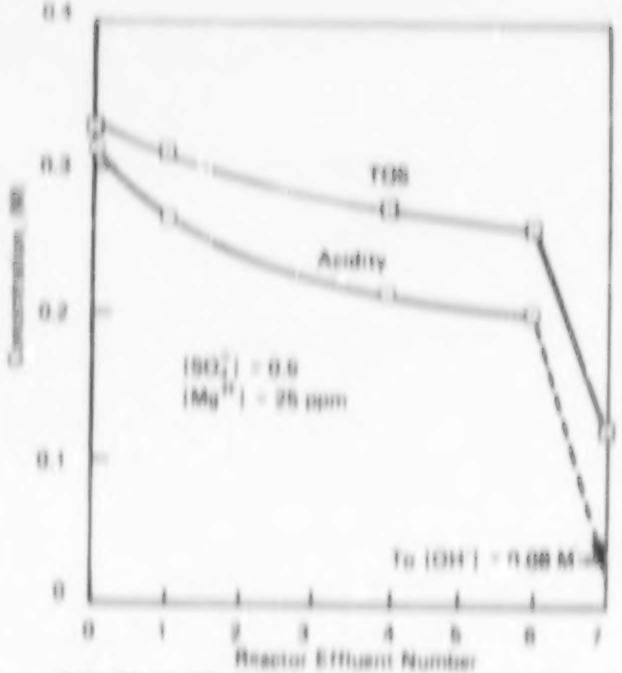


FIGURE VI-22 RUN 124 (HIGH SULFATE + POST LIMING)

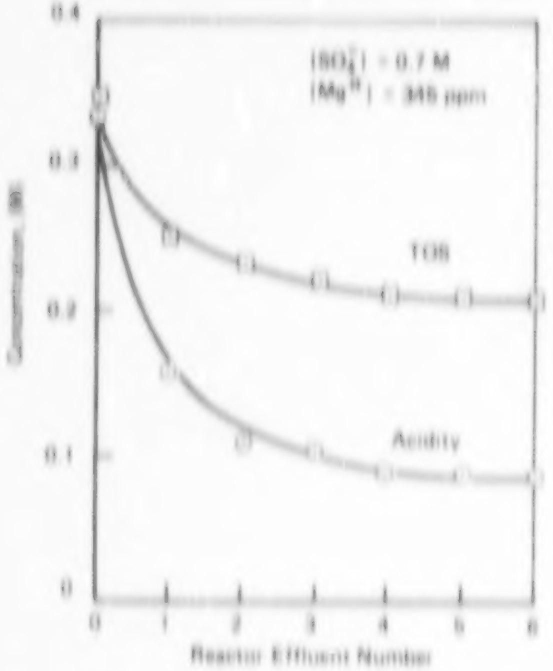


FIGURE VI-23 RUN 127 (SOLIDS RECYCLE)

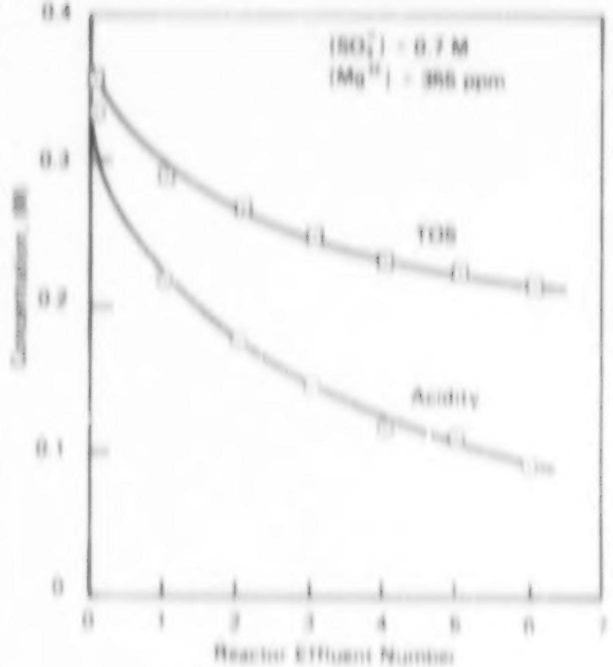


FIGURE VI-24 RUN 128 (EXTENDED HOLDUP)

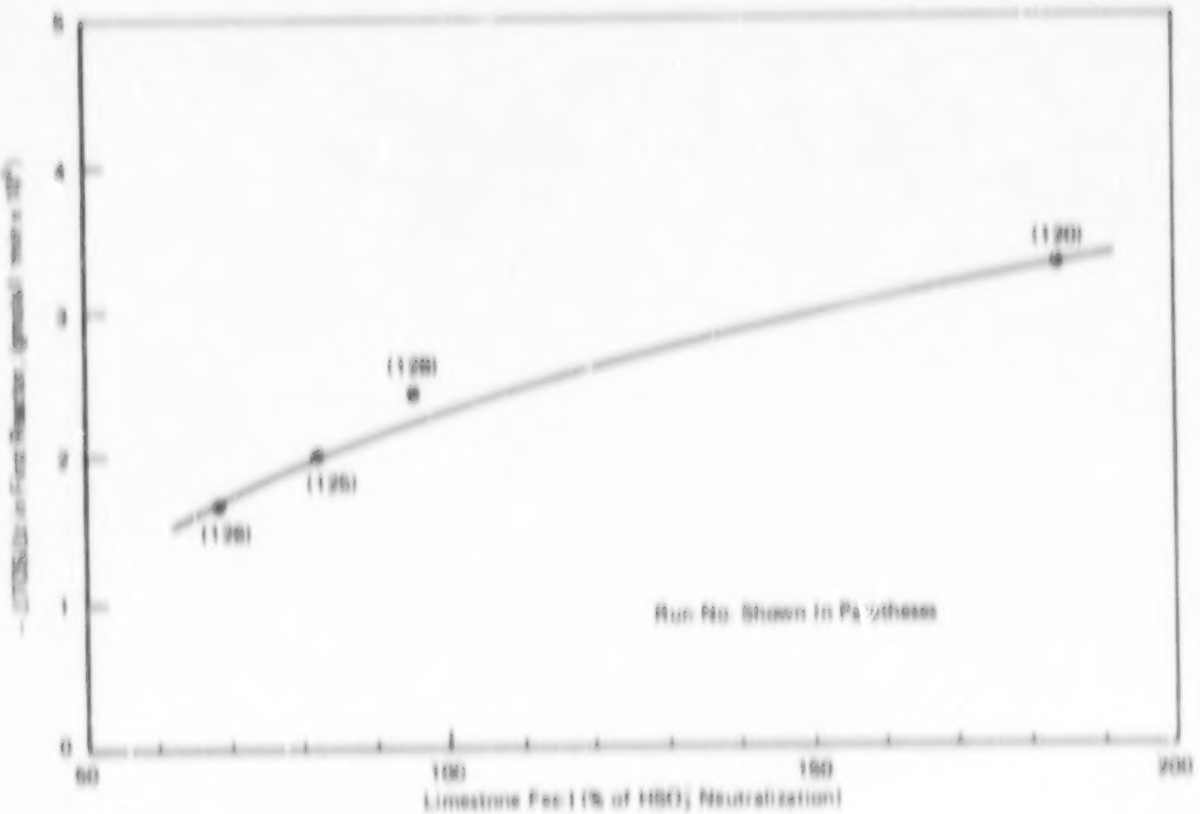


FIGURE VI-25 REACTION RATE VS. LIMESTONE FEED STOICHIOMETRY

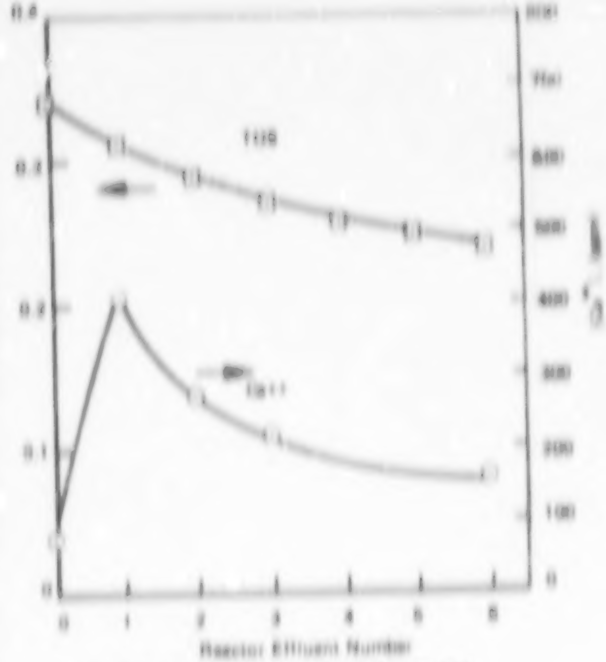


FIGURE VI-26 RUN 125 (BASE CASE)

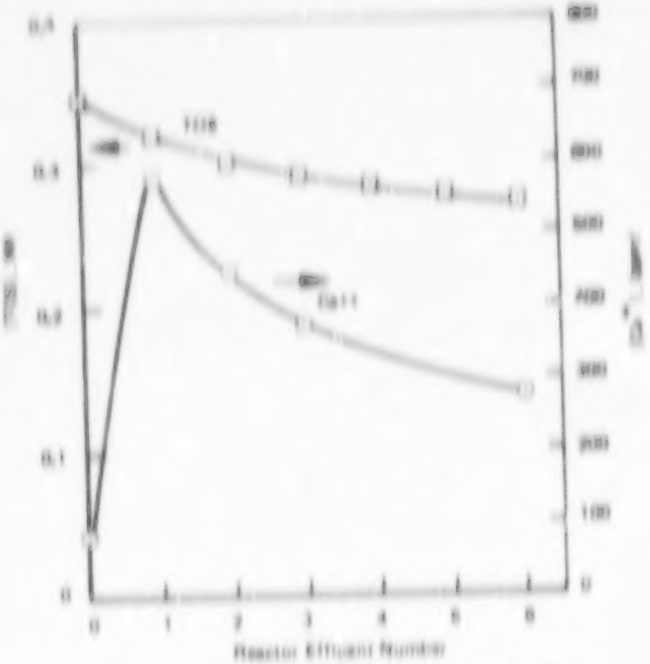


FIGURE VI-27 RUN 126 (LOW $CaCO_3$ FEED)

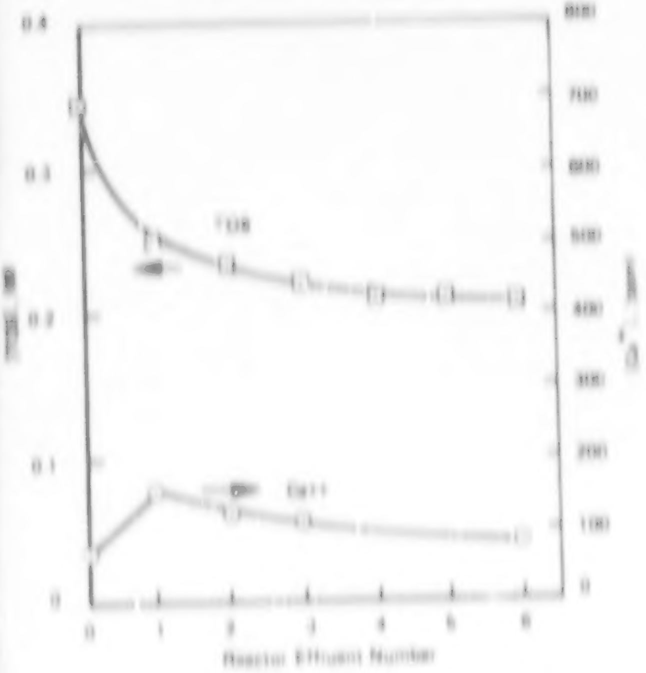


FIGURE VI-28 RUN 127 (SOLIDS RECYCLE)

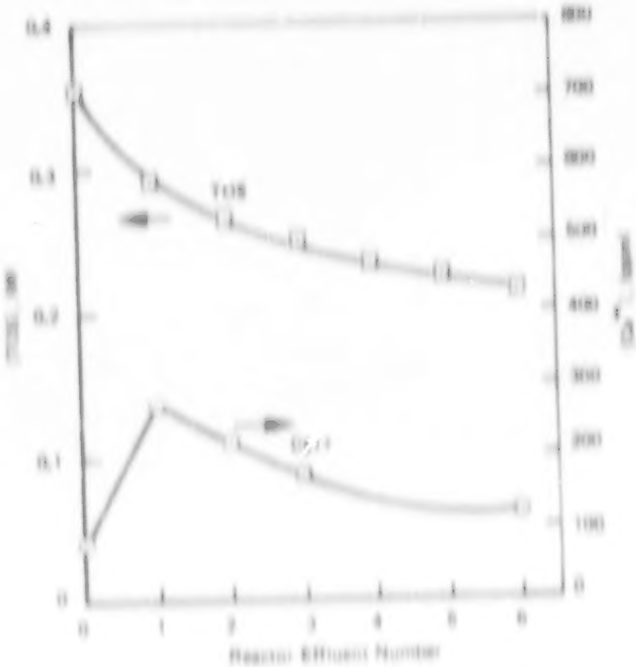


FIGURE VI-29 RUN 128 (EXTENDED HOLDUP)

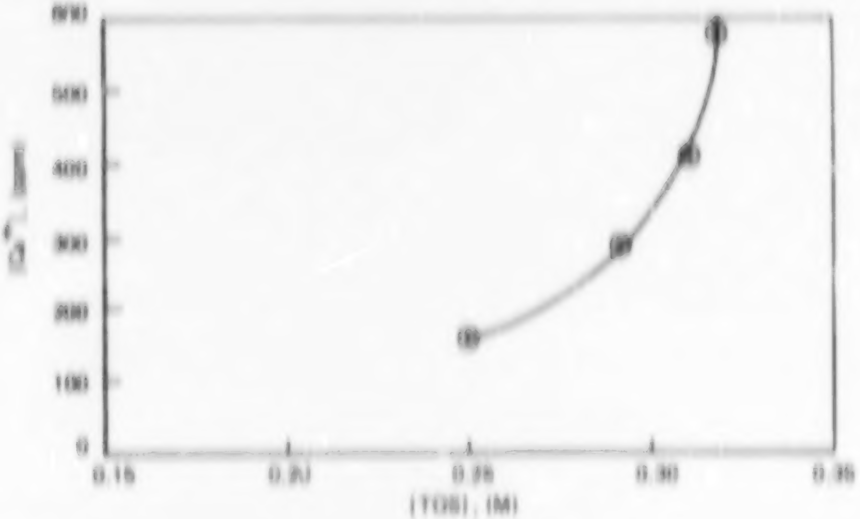


FIGURE VI-30 SOLUBLE CALCIUM VS TOS IN REACTOR 1

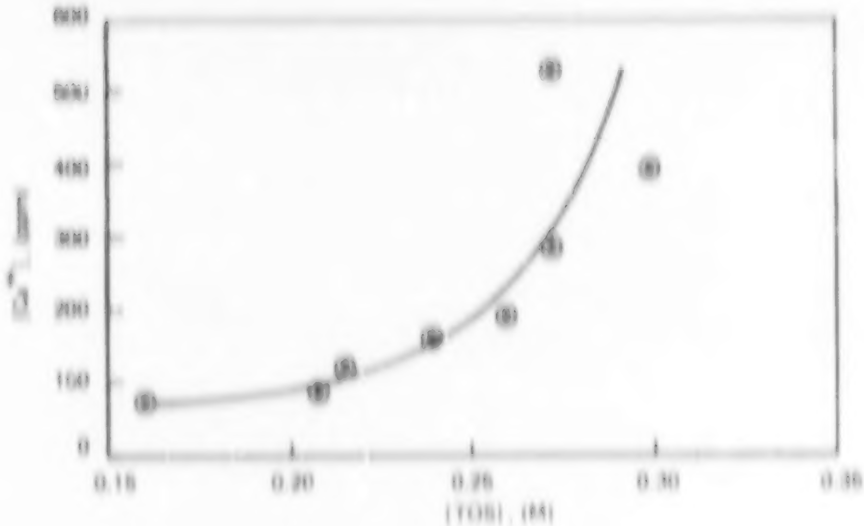


FIGURE VI-31 SOLUBLE CALCIUM VS TOS IN REACTOR 6

all reactors the apparent solubility products are higher than those predicted by the method of Kusik and Meissner, as in the concentrated lime mode (see Figure VI-12). This could reflect supersaturation, inaccuracy in the predicted curve, and/or the fact that the solubility product curve for pure calcium sulfite does not apply to the combined calcium sulfite/sulfate solids produced.

It is interesting that the apparent solubility product for the high magnesium run is greater than those of any of the other runs even when low estimates of sulfite concentration are used. This may result from interference of magnesium in calcium sulfite precipitation.

Dewatering Properties of the Waste Solids

The settling curves for the solids produced in these runs are shown in Figures VI-33 through VI-40.

In general, the settling properties of the solids produced deteriorated with increasing solids holdup time, as seen in runs 127 and 128. The solids properties in run 127 (with solids recycle) were particularly bad. In 24 hours the solids in the slurry from the last reactor settled only 20%, and the family of settling curves shown in Figure VI-39 show that the settling rates for the solids from all reactors were equally low. The properties of the solids were also reflected in the consistency of the filter cake. The cake produced in run 127 was quite thixotropic in nature, rather than gritty and porous as in most of the other runs, although in many cases the gritty, porous nature of the cake was due to the presence of large quantities of unreacted limestone.

Unfortunately, the relative solids content of the various filter cakes did not follow the trends in the settling data. Most of the filter cakes, including that in run 127, ranged between 35% and 40% solids. However, the solids content data for the filter cake is of questionable significance in these runs, since the unthickened effluent slurry was fed directly to the filter. Because of the low flow and the low solids levels, there were usually not enough solids to completely cover the filter cloth. Therefore, air leakage through open cloth area and thin solids layers frequently resulted in low vacuum and poor dewatering.

The deterioration of settling properties with increasing solids holdup, as seen in runs 127 and 128, is consistent with behavior observed in laboratory batch experiments. Settling time in the batch experiments tended to increase as the run progressed even after most of the reaction was complete. It would appear that the major effect is one of holdup time, but it is difficult to divorce limestone utilization or extent of reaction, since these tend to go hand-in-hand.

The effects of high magnesium and sulfate concentrations in these runs are primarily on reaction rates. Since there was little reaction, the solids produced were primarily limestone and therefore exhibited reasonably good settling rates. However, in all cases of high sulfate or

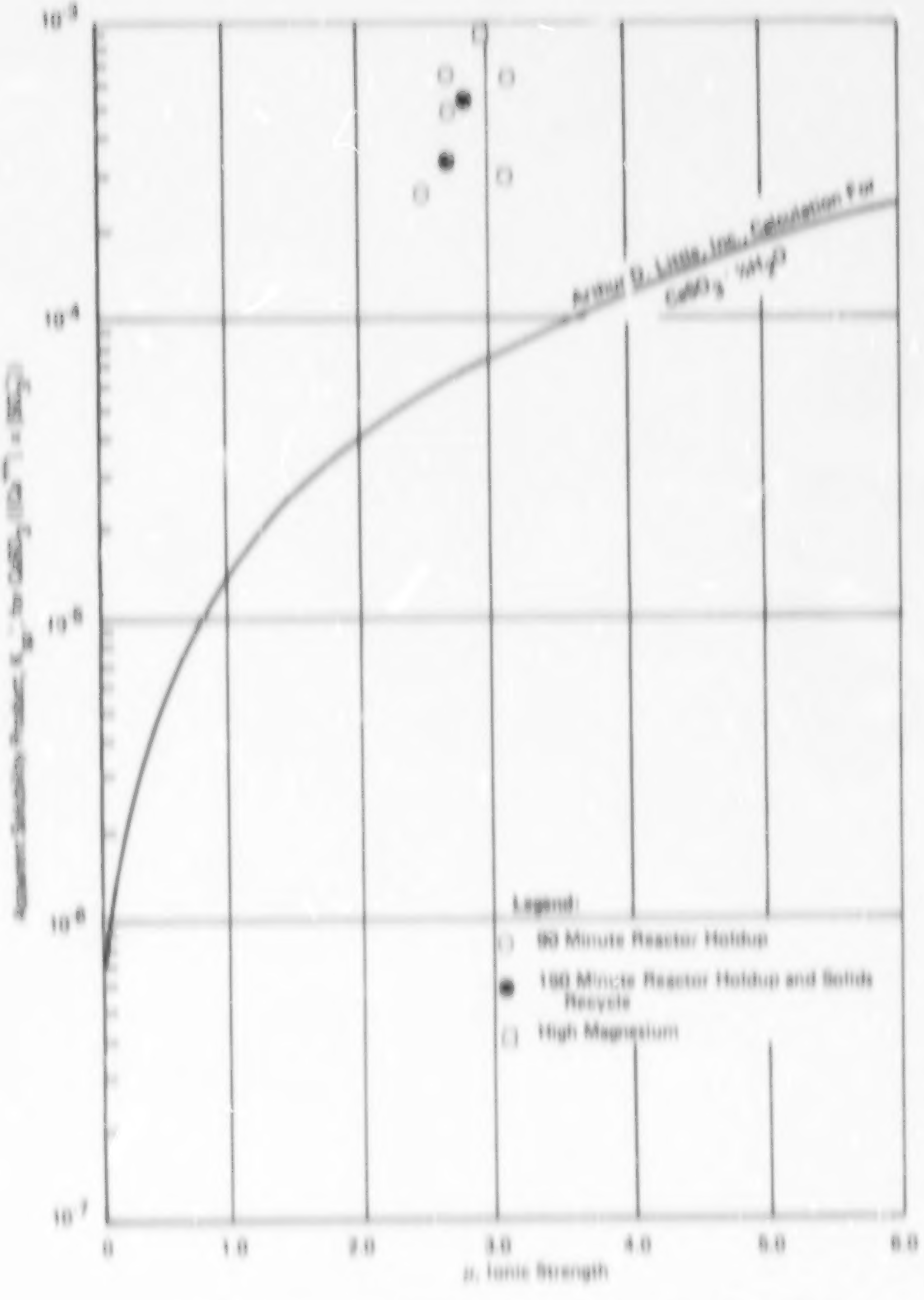


FIGURE VI-32 RELATION OF OBSERVED APPARENT SOLUBILITY PRODUCTS TO SATURATION VALUES FOR $CaSO_3$

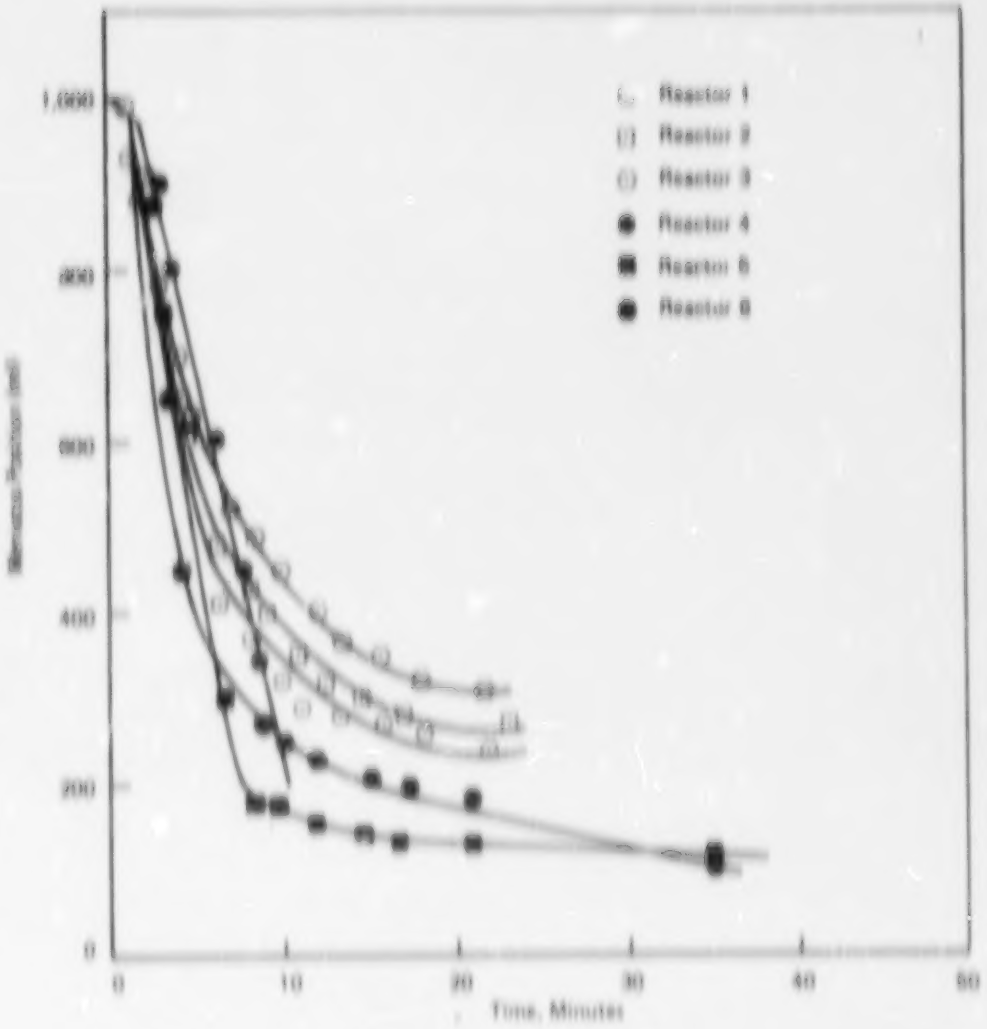


FIGURE VI-33 SETTLING CURVES FOR RUN 105 – BASE RUN

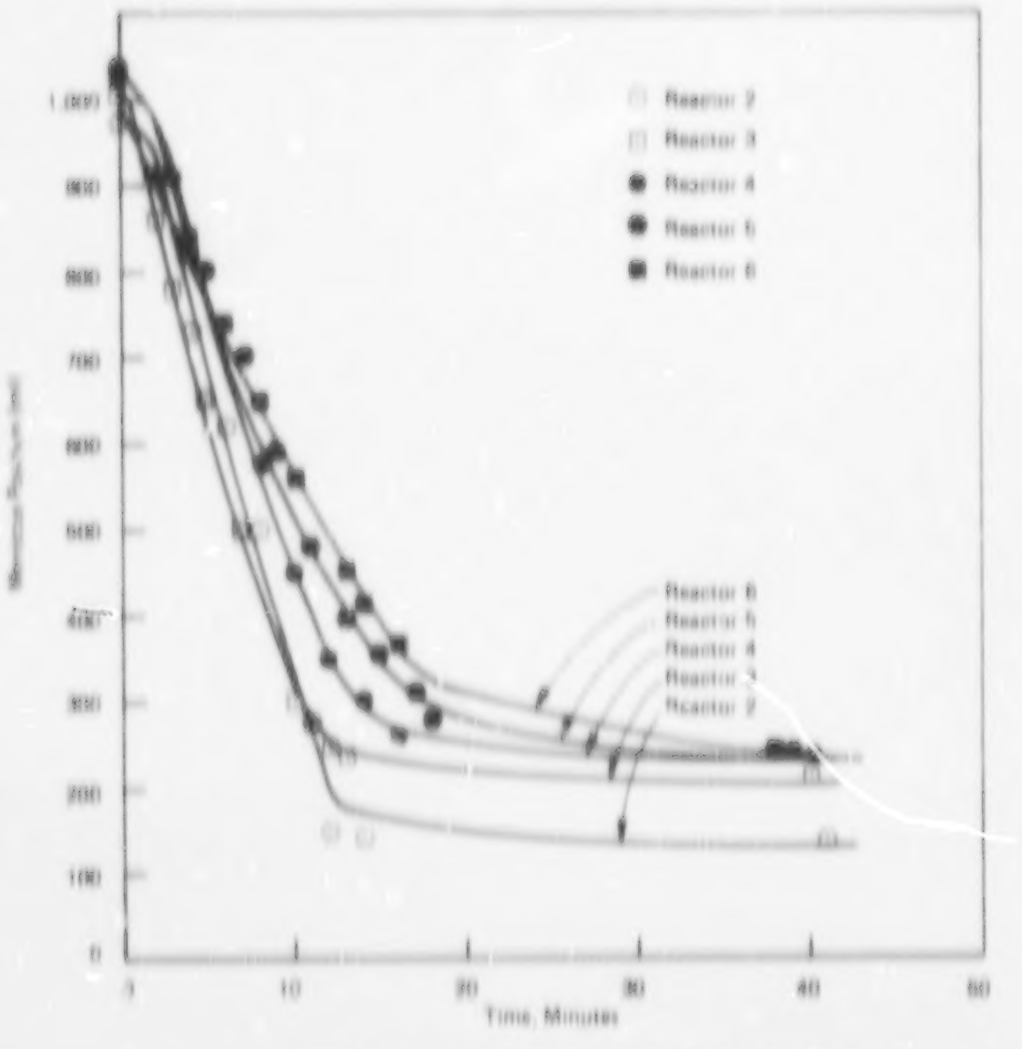


FIGURE VI-34 SETTLING CURVES FOR RUN 120

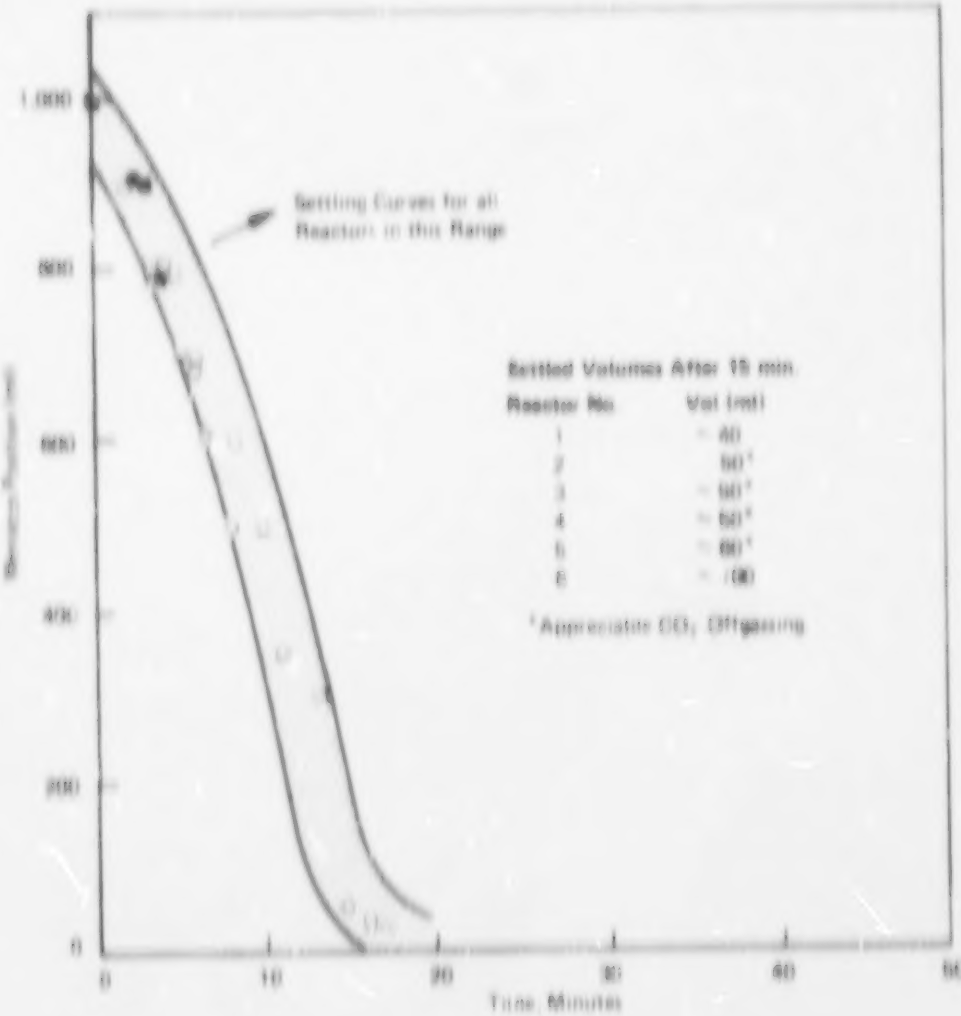


FIGURE VI-26 SETTLING CURVES FOR RUN 101

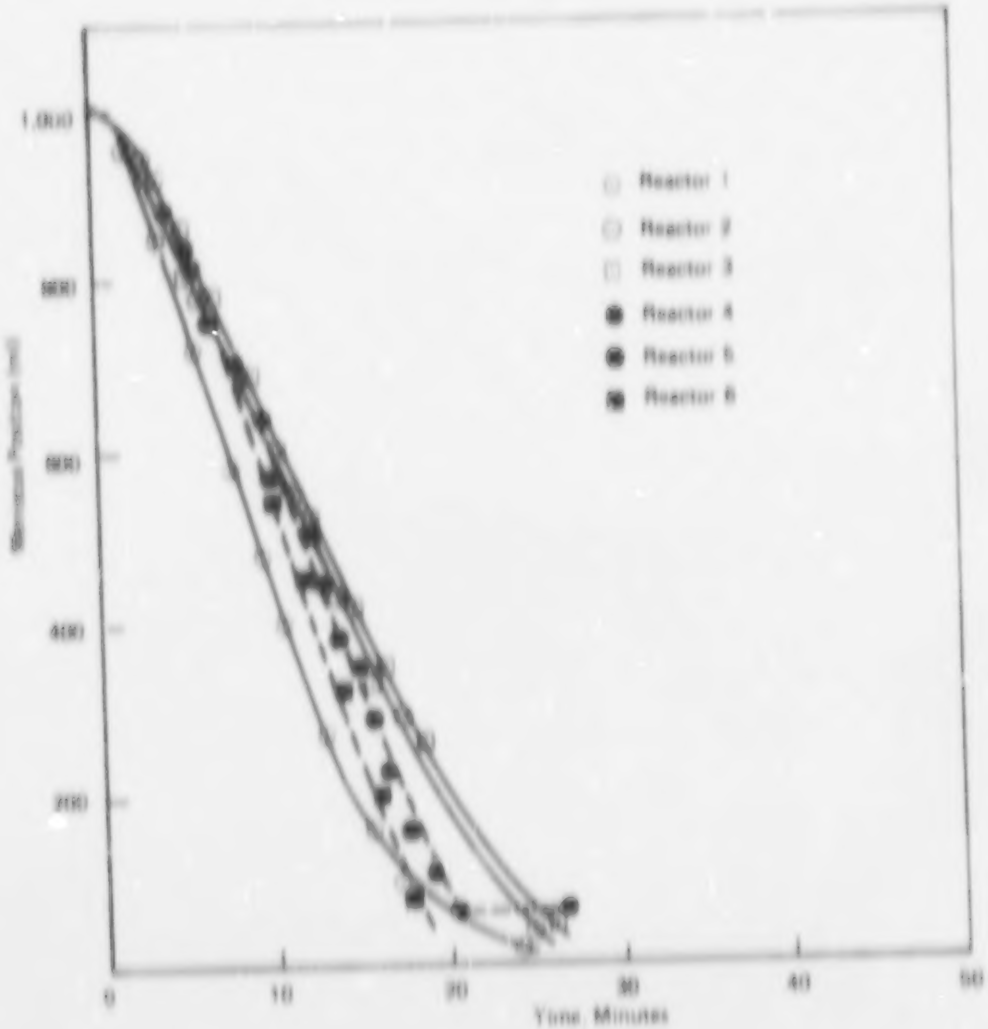


FIGURE VI-36 SETTLING CURVES FOR RUN 123

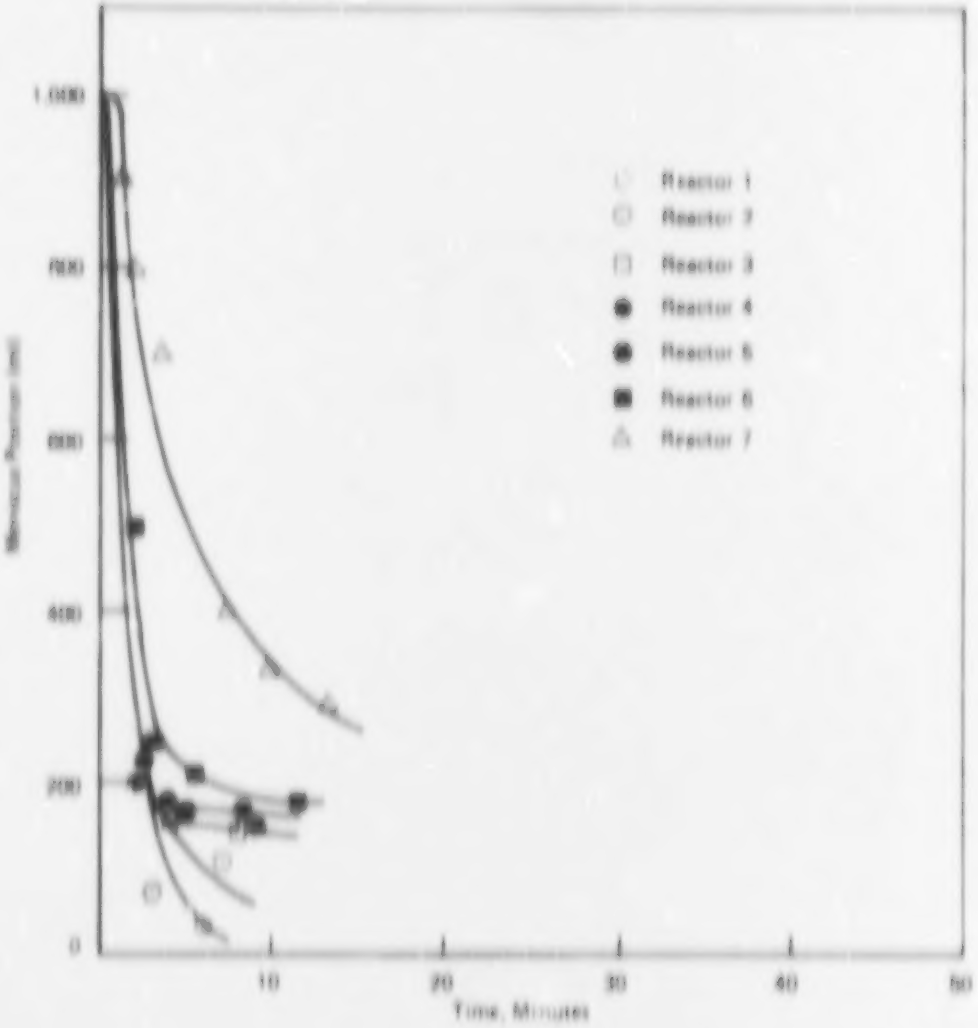


FIGURE VI-37 SETTLING CURVES FOR RUN 124

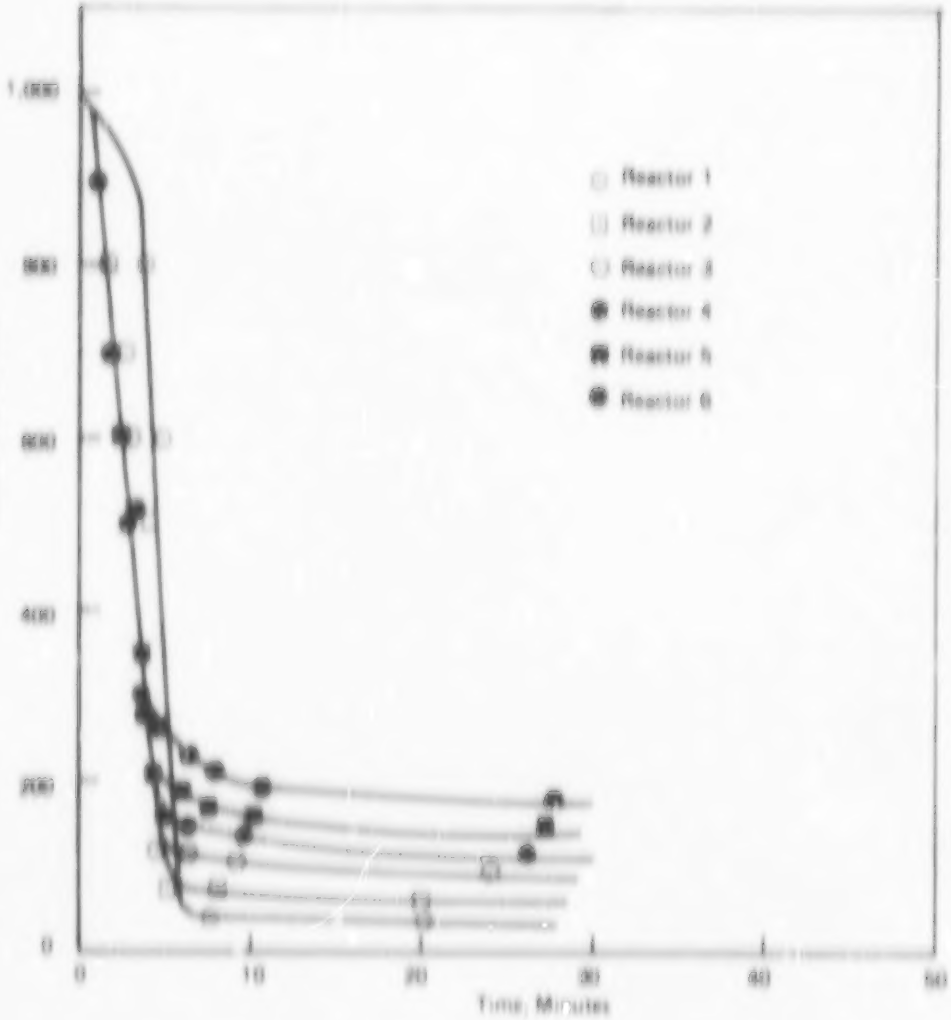


FIGURE VI-38 SETTLING CURVES FOR RUN 126

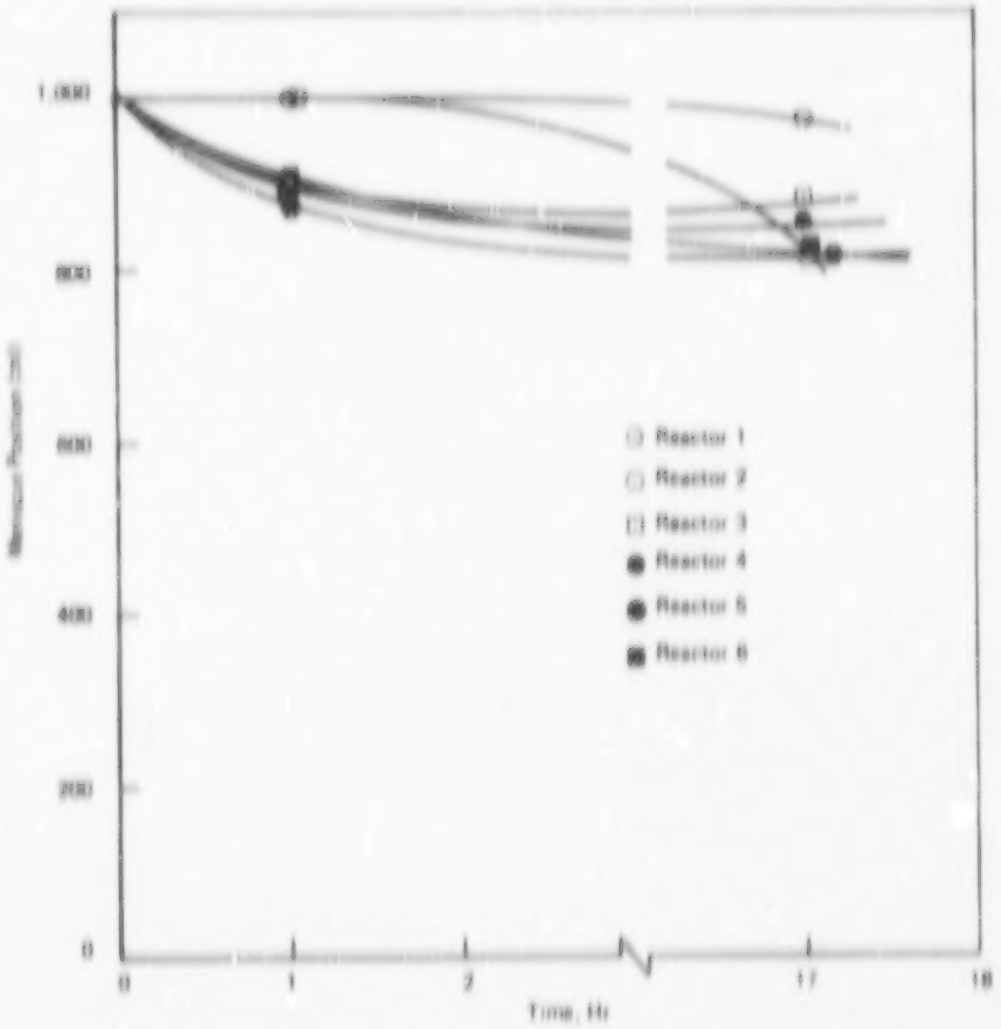


FIGURE VI-38 SETTLING CURVES FOR RUN 127

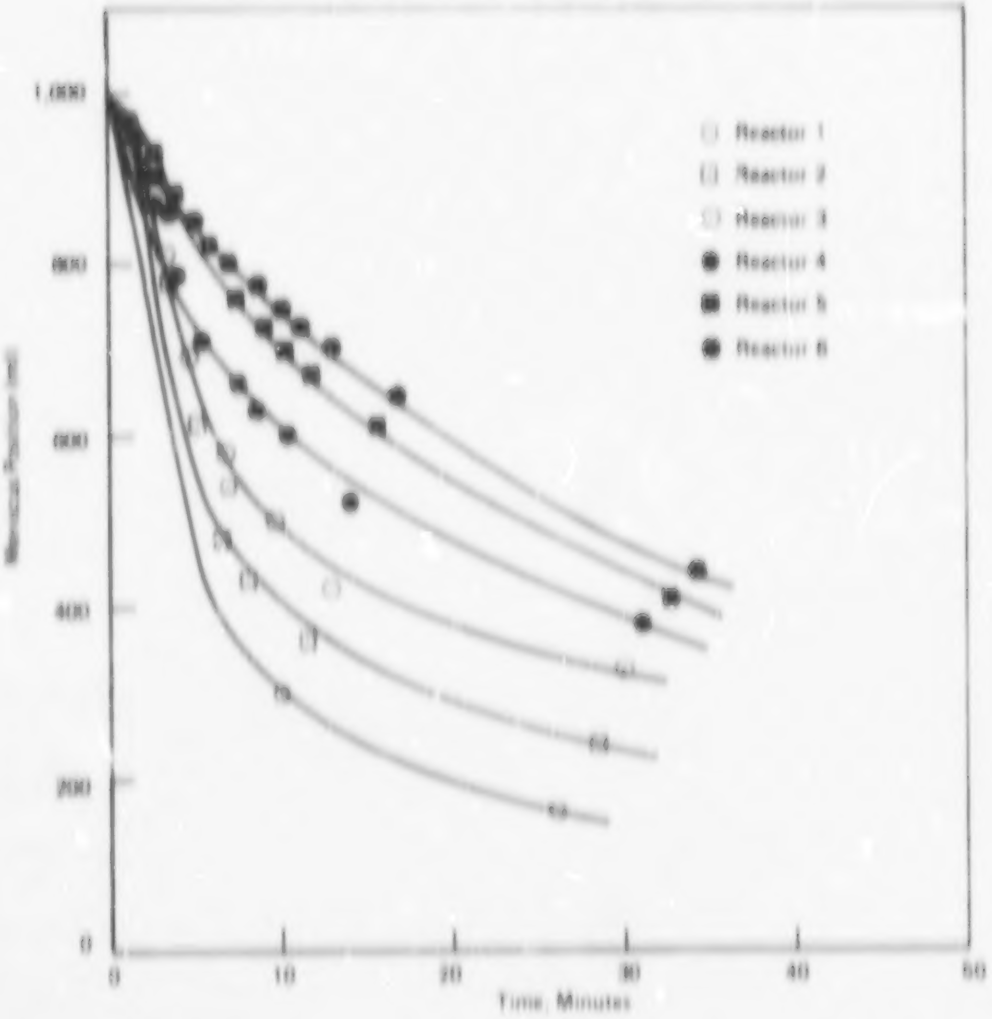


FIGURE VI-40 SETTLING CURVES FOR RUN 126

magnesium (runs 121, 123 and 124) the solids settling rates were noticeably slower than in runs 125 and 126, where limestone utilizations were significantly higher, and were only comparable to that in run 120 (high limestone feed) because the high solids content of run 120 resulted in hindered settling.

In all runs except 120, 127, and 128 there was appreciable off-gassing of CO_2 in all of the reactors. This off-gassing was also apparent in the settling test performed on the reactor effluent slurries. For the most part, the degree of off-gassing (or bubbling) decreased with increased bisulfite conversion. Thus, in runs 121, 123 and 124 there tended to be more bubbling in the last few reactors than in runs 125 and 126. This bubbling suggests that better than 75% utilization of limestone will be required in the reactor system to avoid poor clarity in the thickener overflow. Otherwise, special provisions will have to be made to circumvent solids carryover to the scrubber system.

Magnesium Dissolution

Since soluble magnesium has an important deleterious effect on reaction rate, magnesium dissolution from the limestone and the projected steady-state soluble magnesium concentration is of concern. The soluble magnesium concentration may depend upon a number of factors including the amount of magnesium in the limestone, its rate of dissolution, the purge rate of soluble magnesium in the filter cake, and the solubility of magnesium sulfite.

The Fredonia limestone used in these runs contained 0.14-0.19 mmole of magnesium per gram of dry limestone. If all of this could dissolve, then the concentration of magnesium attained in the liquor would be determined by the solubility of magnesium sulfite and could exceed 3,000 ppm. However, the amount of magnesium dissolved varied with the magnesium concentration in the liquor and solids holdup. In all runs at less than 500 ppm magnesium and 90 minutes total holdup, 30% to 50% of the magnesium in the limestone dissolved, resulting in increases of 20 to 40 ppm of magnesium in the liquor. At the same inlet liquor concentrations but with solids recycle or a 180-minute reactor holdup (runs 127 and 128) about 75% of the soluble magnesium dissolved, resulting in increases in magnesium in the solution of about 60 ppm across the reactor system. And at 2,250 ppm magnesium with 90 minutes holdup there was no appreciable dissolution of magnesium (run 121), although there was also very little reaction of the limestone, which may have limited dissolution of magnesium.

These data suggest that with Fredonia limestone operating at 0.3-0.4 M TOS and at a temperature of 50± 5°C, the soluble magnesium concentration will not exceed about 2,000 ppm in steady-state operation. However, at these concentrations, utilization is seriously reduced. One possible measure that can be taken to decrease magnesium levels, as discussed previously, is to treat the limestone reaction effluent with lime to raise the pH above 10. This will precipitate magnesium as

$Mg(OH)_2$ and prevent the buildup of soluble magnesium. The merits of such an approach depend upon the amount of lime required and the associated system costs. As a test of post-liming in the open-loop runs, product liquor was reacted with lime to a pH slightly above 11 in a 30 minute CSTR (run 1/4). The solids produced had acceptable settling properties and the magnesium level in the solution was decreased essentially to zero. However, the pH was difficult to control and in a large-scale system care would have to be taken to fine-tune lime feed rates, or an intermittent lime feed system would have to be used.

Calcium Sulfate Precipitation

The precipitation of calcium sulfate in the concentrated limestone mode is even more important than in the concentrated lime mode. The limestone utilization is much more sensitive to high sulfate concentration than is lime utilization, and limiting sulfate concentration, thereby limiting calcium sulfate precipitation rates, can severely restrict the applicability of a limestone dual alkali system.

In Figure VI-41 the ($CaSO_4/CaSO_3$) ratio in the product solids is plotted as a function of the ratio of ($[SO_4^=]/[SO_3^=]$) in the reactor system effluent liquor. Included in this plot are a number of points from the closed-loop runs. Over a reasonable operating range of soluble sulfate (up to sulfate-to-sulfite ratio of about 10:1) the typical calcium sulfate precipitation can be approximated by the following equation:

$$\left(\frac{CaSO_4}{CaSO_3}\right)_{\text{reactor solids}} = 0.022\left(\frac{[SO_4^=]}{[SO_3^=]}\right)_{\text{reactor liquor}} \qquad (3)$$

This rate of calcium sulfate precipitation is only about 60% of that in the concentrated lime mode as shown in Figure VI-41 and by comparison of equation (3) with equation (1). The lower calcium sulfate precipitation may be due to the slower reaction rate over the range of TOS studied ([TOS] = 0.3-0.4M) than in the lime regeneration. This slower rate may allow a closer approach to equilibrium. (In this regard, it is recalled that in the concentrated lime mode there was a slight redissolution of calcium sulfate with long solids-liquid holdup times following the reactor system.)

The implication of this lower level calcium sulfate precipitation is clearly that limestone dual alkali systems operating in this range of TOS will be limited to applications where low oxidation rates are expected, unless means are found to increase limestone reaction rates (which may also increase sulfate precipitation).

2. Closed-Loop Runs

Four closed-loop runs in the concentrated limestone mode were made with active sodium levels ranging from 0.27M to 0.45M and inlet SO_2 levels ranging from 2,100 ppm to 2,800 ppm. All of these runs involved multi-stage reactor systems consisting of anywhere from two to five CSTR's in

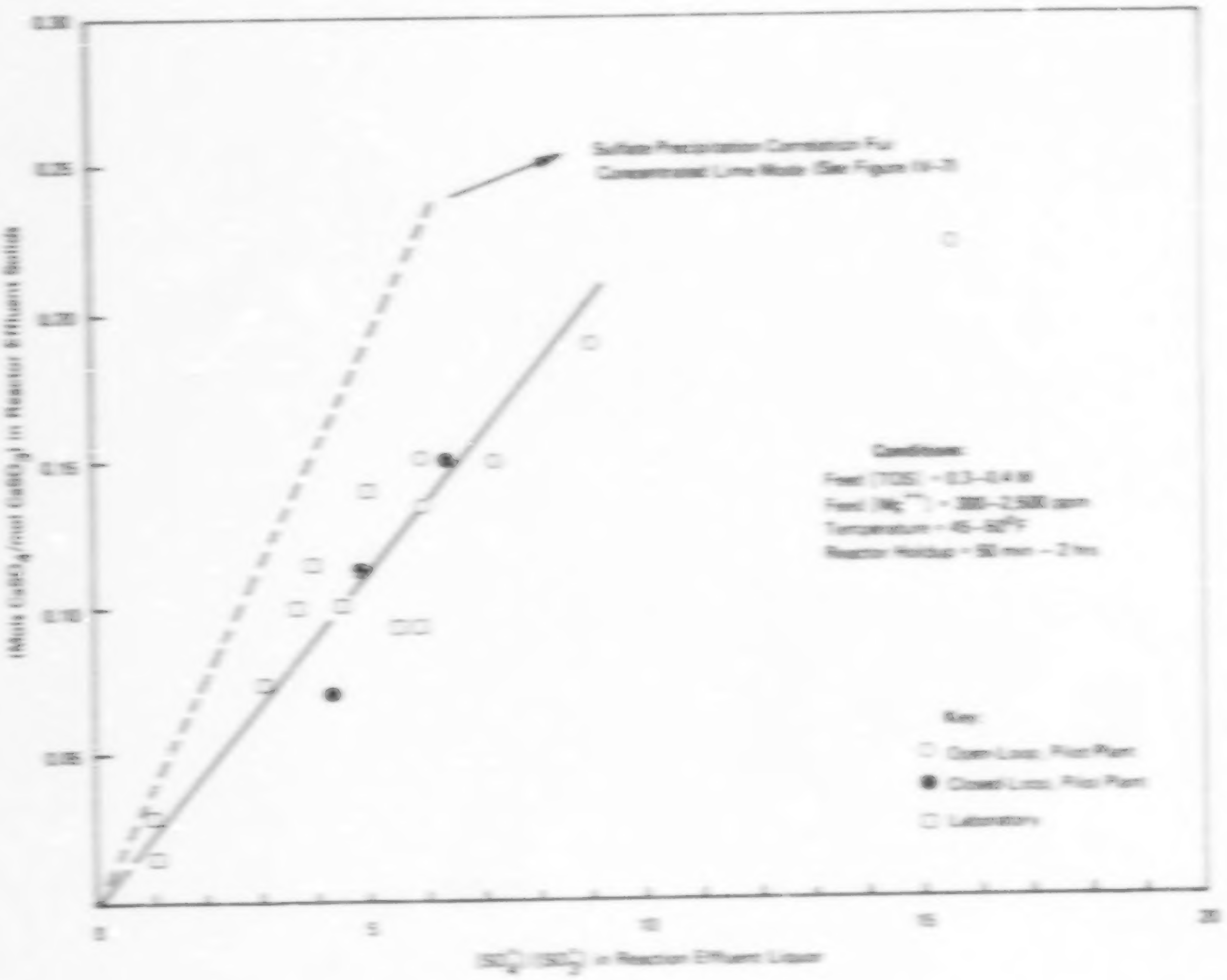


FIGURE VI-47 SULFATE PRECIPITATION IN THE CONCENTRATED LIMESTONE MODE

series. Except for the reactor system, the equipment configuration and utilization were identical to that of concentrated lime mode operations. Figure VI-42 gives a schematic of the system configuration and Table VI-9 summarizes the general operating conditions and key performance parameters for the four runs.

While overall limestone utilization and SO_2 removal were reasonably high in all runs, none of the runs can be considered successful. In every case the solids produced exhibited poor settling properties. After about one day of operation in each run, solids began overflowing the thickener and were carried forward to the scrubber system. The quantity of solids in the overflow increased continuously with time to the point that the system became a combination of direct limestone/dual alkali process. The presence of high levels of suspended solids in the scrubber system undoubtedly accounts for the very high limestone utilization factors, as evidenced by the analyses of the solids in the scrubber bleed slurry. Not only does some unutilized limestone react in the scrubber system, but the carryover of solids into the scrubber results in an overall solids recycle throughout the system, allowing higher solids residence time and longer solids/liquid contact.

Figures VI-43 and VI-44 show process operating diagrams for runs 411 and 430, two runs in which there were sufficiently stable periods when the system operation and performance could be evaluated quantitatively. It must be stressed that the data in these figures represent "snapshots" of the process operation rather than steady-state conditions. In all runs the overflow of solids from the thickener increased with time, eventually necessitating shutdown of the system.

The causes for the poor settling solids and carryover in the thickener overflow differed according to operating conditions. In general, though, there were four factors of obvious significance:

- High soluble iron concentrations -- In run 430 high soluble iron concentrations (up to 400 ppm) apparently from dissolution of the iron oxide coating in the thickener and feed forward surge tank initially retarded reaction rates to the extent that it was not possible to regenerate to a pH greater than 5.8 even with four reactors; and limestone utilizations were less than 35%. This resulted in excessive bubbling in the thickener (CO_2 off-gassing) due to continuing reaction.

  The iron was virtually eliminated by switching from limestone to lime. After three days of operation with lime, the solids properties noticeably improved. The solids settling rate increased; the level of suspended solids in the thickener overflow decreased to less than 500 ppm; and the filtration rate increased from a few pounds of cake per hour to over 200 pounds per hour. The solids content of the filter cake also rose to about 45%.

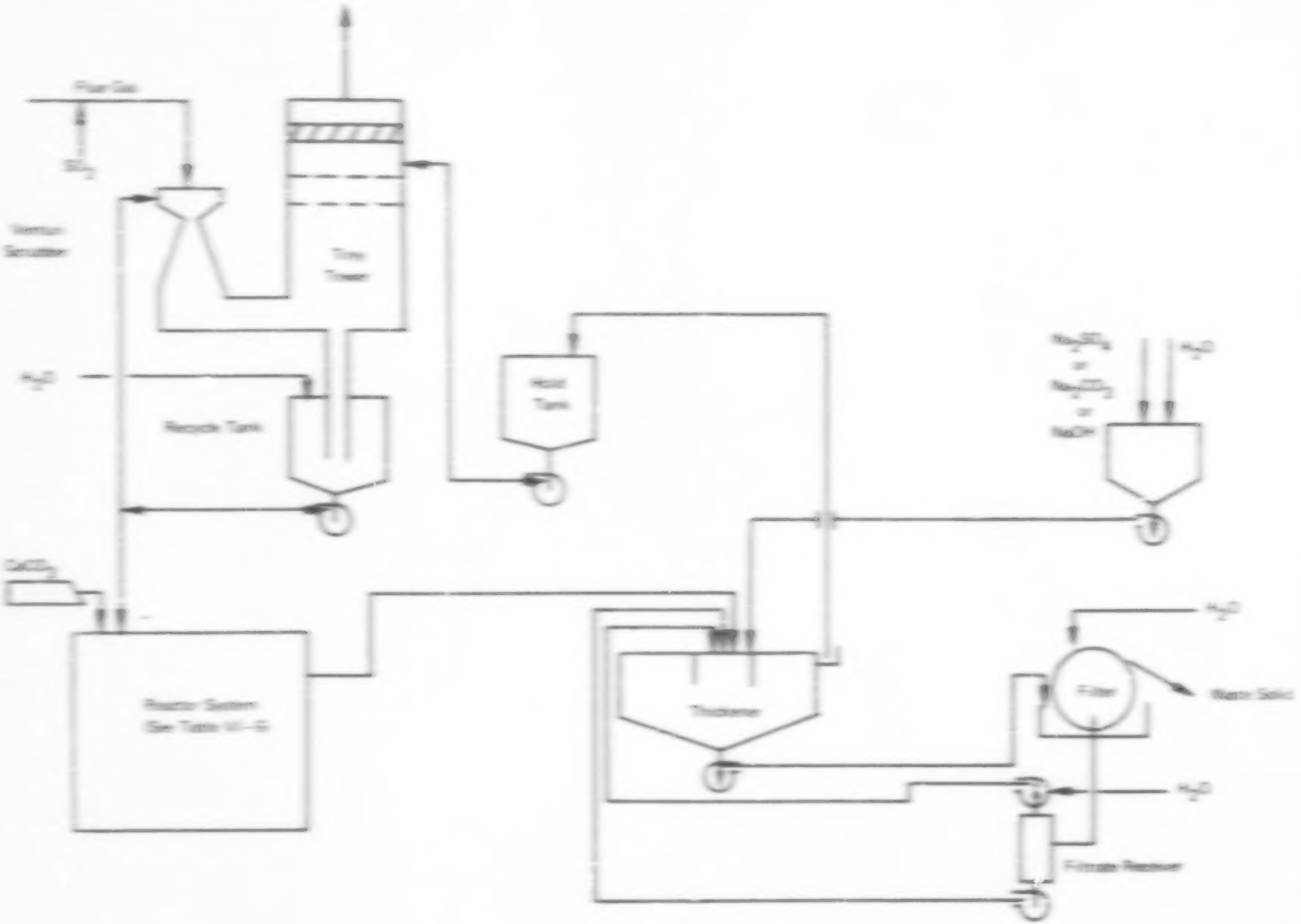

Flue Gas
SO_2
Venturi Scrubber
Tray Tower
H_2O
Recycle Tank
Hold Tank
Na_2SO_4 or Na_2CO_3 or NaOH
H_2O
$CaCO_3$
Reactor System (See Table VI-6)
Thickener
H_2O
Filter
Waste Solid
H_2O
Filtrate Receiver

FIGURE VI-4C PROCESS FLOW DIAGRAM FOR CONCENTRATED LIMESTONE MODE PILOT PLANT OPERATIONS CONTINUOUS CLOSED-LOOP

TABLE VI-4

SUMMARY OF CLOSED-LOOP RUNS USING MULTISTAGE REACTOR SYSTEMS

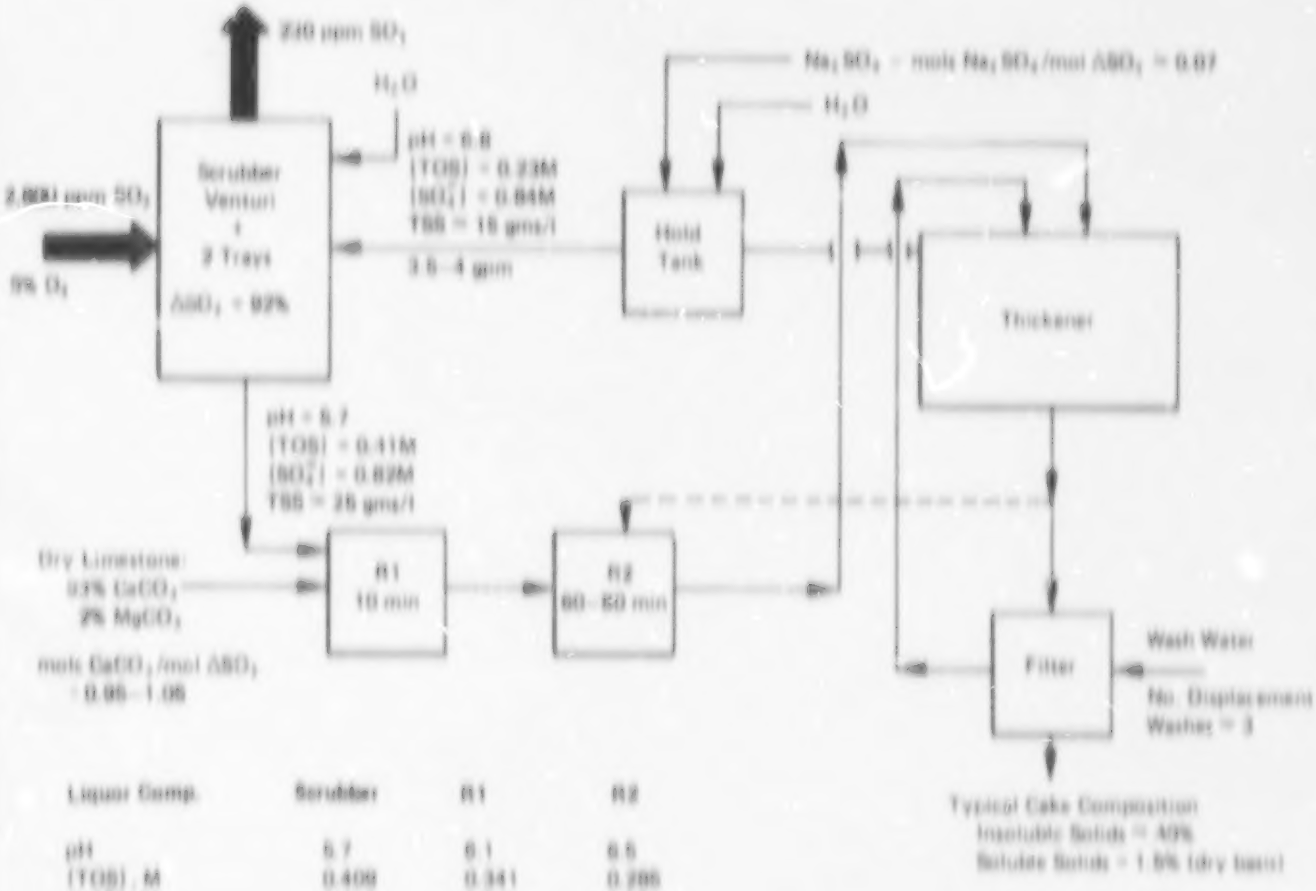
Run No.	420	421	422	430
Run Duration, (days)	2.5	2.5	3	6.5
Operating Conditions				
Inlet Gas:				
SO_2, (ppm)	2,400	2,800	2,300	2,300
O_2, (vol. %)	4	5	4.5-5.5	4-5
Temperature, (°F)	370-415	370-415	360-375	355-390
Scrubber Bleed:				
pH	5.5-6.4	5.6-5.9	5.0-6.0	5.3-6.1
[Na+], (M)	0.4	0.37-0.4	0.25	0.5^c
$[SO_4^=]$, (M)	0.85	0.6-0.85	0.7	0.6-0.7^c
[illegible]	<1	up to 1.5^a	<2	2-3
Reactor System:				
No. Reactors x Holdup, (min.)	1 x 7 + 1 x 70	1 x 20 + 1 x 150-400	3 x 25 + 1 x 30	1 x 6 + 12 or 21 x 17
Solids Recycle to Reactor	No	Intermittent	No	No
Chemical Makeup:				
Sodium	Na_2CO_3	Na_2CO_3	Na_2CO_3	NaOH
Limestone	Fredonia	Fredonia	Fredonia	Fredonia
Key Results				
SO_2 Removal, (% of inlet)	96	90-95	85	90
Sodium Feed Rate, mole Na_2^{++}/(mol ΔSO_2 + Na_2SO_4)	0.10	0.07	0.03	0.10
Calcium Feed Rate, mole $CaCO_3$/(mol ΔSO_2 + Na_2SO_4)	1.1	0.95-1.05	1.0-1.05	0.95-1.0
(% to neutralize HSO_3^-)	105	125-145^a	120	75
Calcium Utilization, (% of $CaCO_3$)	48	80-90	92	95
Soluble Calcium in Reactor Effluent, (ppm)	110	60-140	240	-
Scrubber System Oxidation, (mole % of SO_2)	<200	_b	_b	_b
Filter Cake:				
wt % Insoluble Solids, (avg.)	33	35	40-45	30
wt % Soluble Solids, (avg.-dry basis)	13	11	1.5	2.1
No. Displacement Washes, (typical)	0.5-1		~1	1.5-2
mole $CaSO_4$/mol $CaSO_3$, (avg.)	0.12	0.09	0.09	0.11

---

[a] During Run 421 there was significant carryover of solids in the thickener overflow due to the poor settling properties of the solids. The amount of solids increased during the run. When the system was shut down, the venturi bleed contained 1.5% suspended solids. This carryover of solids undoubtedly accounts for the high utilizations achieved since unused limestone reacted in the scrubber system. This also accounts for the artificially high $CaCO_3$/(HSO_3^-) feed ratio to the reactor, since some of the SO_2 precipitated in the scrubber (reducing the liquor feed forward rate).

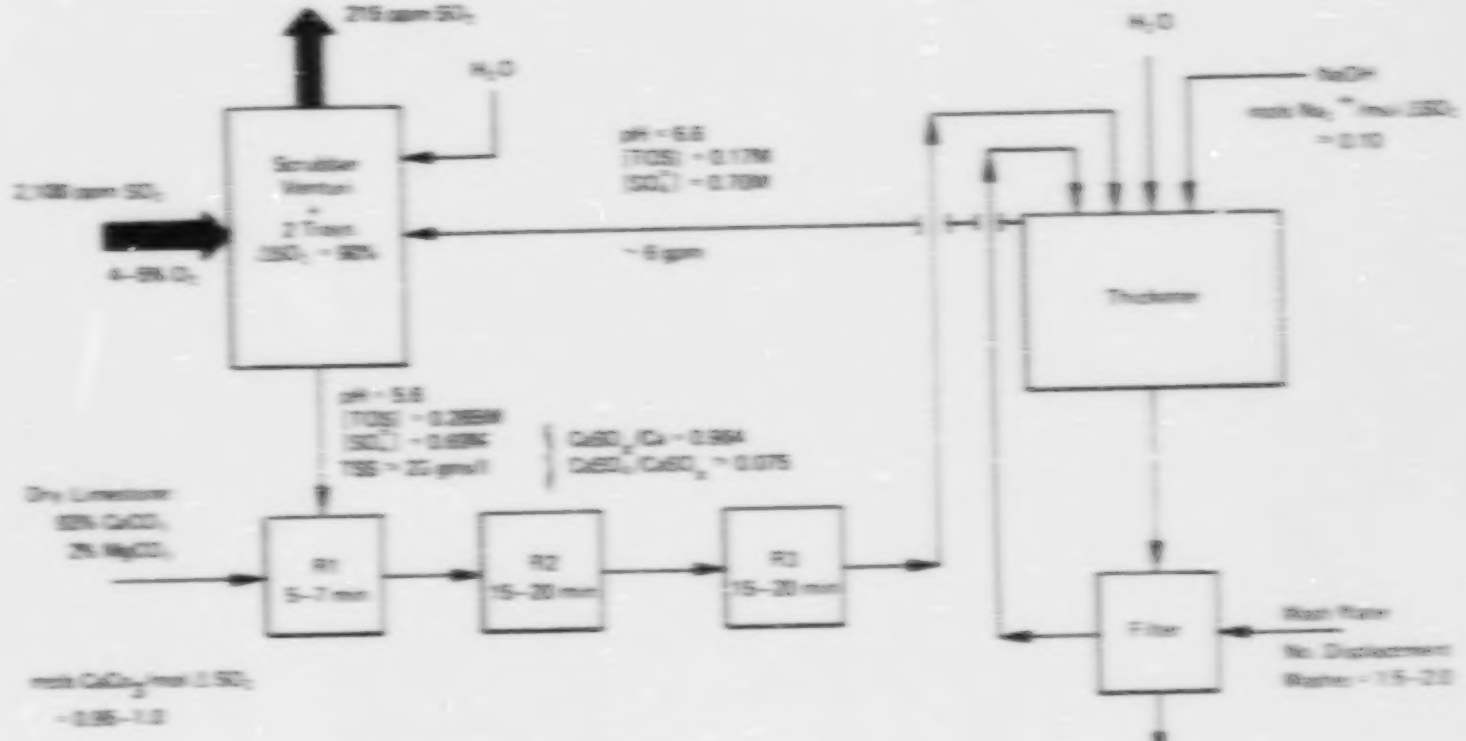
[b] Oxidation rates could not be estimated due to the presence of a variable amount of solids in the scrubber system.

[c] Average concentrations maintained by a number of system upsets and dumping of the Na_2SO_4 during the run.


230 ppm SO_2
H_2O
Na_2SO_4 – mols Na_2SO_4/mol ΔSO_2 = 0.07
H_2O
2,800 ppm SO_2
9% O_2
Scrubber
Venturi
+
2 Trays
ΔSO_2 = 92%
pH = 6.8
[TOS] = 0.23M
[$SO_4^=$] = 0.84M
TSS = 15 gms/l
3.5–4 gpm
Hold
Tank
Thickener
pH = 5.7
[TOS] = 0.41M
[$SO_4^=$] = 0.82M
TSS = 25 gms/l
Dry Limestone:
93% $CaCO_3$
2% $MgCO_3$
mols $CaCO_3$/mol ΔSO_2
= 0.95–1.05
R1
10 min
R2
60–80 min
Filter
Wash Water
No. Displacement
Washes = 3
Typical Cake Composition
Insoluble Solids = 40%
Soluble Solids = 1.5% (dry basis)

Liquor Comp.	Scrubber	R1	R2
pH	5.7	6.1	6.5
[TOS], M	0.408	0.341	0.285
[$SO_4^=$], M	0.819	0.817	0.804
TSS, gms/l	40	61	70
Iron, ppm	–	–	–
[Mg^{++}], ppm	≈ 125	–	–
Solids Comp:			
$CaSO_3$/Ca	≈ 1.0	0.72	0.80
$CaSO_4$/$CaSO_3$	0.14	0.12	≈ 0.1

FIGURE VI-43 SYSTEM OPERATION IN RUN 411 (AFTER 35 HRS)


215 ppm SO₂
H₂O
Scrubber
Venturi
+
2 Trays
ΔSO₂ = 90%
2,100 ppm SO₂
4–8% O₂
pH = 6.6
[TOS] = 0.17M
[SO₄⁼] = 0.70M
~6 gpm
pH = 5.6
[TOS] = 0.285M
[SO₄⁼] = 0.69M
TSS = 25 gms/l
CaSO₃/Ca = 0.964
CaSO₄/CaSO₃ = 0.075
Dry Limestone
93% CaCO₃
2% MgCO₃
R1
5–7 min
R2
15–20 min
R3
15–20 min
mols CaCO₃/mol ΔSO₂
= 0.95–1.0
H₂O
NaOH
mols Na₂⁺⁺/mol ΔSO₂
= 0.10
Thickener
Filter
Wash Water
No. Displacement
Washes = 1.5–2.0
Cake Composition
Insoluble Solids = 30%
Solubles = 2.1% (dry basis)

Liquor Comp.	Scrubber	R1	R2	R3
pH	5.6	6.1	6.4	6.5
[TOS], M	0.285	0.234	0.197	0.194
[$SO_4^=$], M	0.69	0.705	0.71	0.70
TSS, gms/l	25	35	42	42
Iron, ppm	8	—	—	3
[Mg^{++}], ppm	244	—	—	252
Solids Comp:				
$CaSO_3$/Tot. Ca	0.964	0.92	—	0.95
$CaSO_4$/$CaSO_3$	0.075	0.0635	—	0.084

FIGURE VI-44 SYSTEM OPERATION IN RUN 420 (AT TERMINATION OF RUN)

At this point the lime feed was stopped and the limestone feed resumed. Solids properties again deteriorated. Solids began overflowing the thickener, and the filter cake solids content fell to about 30%. However, the reactor system effluent pH was maintained above 6.3 and soluble iron rose only to a maximum of 8 ppm. Throughout run 430 sodium hydroxide was used for sodium makeup rather than sodium sulfate or soda ash in the hope that the additional alkalinity would minimize soluble iron.

The progression of solids quality prior to, during, and after the lime feed is shown in Figures VI-45 through VI-50. During lime feed, agglomerates of needles were produced which settled reasonably well; however, before and shortly after liming, the needles did not agglomerate, and settled poorly.

- High sulfate-to-active sodium ratios -- In all the closed-loop runs there was a relatively high sulfate-to-active sodium ratio. This was not by design. The sulfate levels in all runs tended to increase due to a combination of factors: makeup with sodium sulfate (runs 410 and 411); low calcium sulfate precipitation rates compared with oxidation; and, apparently, slightly higher oxidation rates in the system due to the additional reactors and pumps.

  The combination of the relatively high sulfate levels and the soluble magnesium (which ranged from 100 ppm to 300 ppm) may have been sufficient, along with a small amount of soluble iron, to affect solids properties. In none of the runs, though, did magnesium or sulfate approach steady-state levels due to the occasional attempts to improve solids properties by repriming the venturi recycle tank and reactors. What is the effect?

- Inappropriate reactor design -- In runs 410 and 411 the reactor system consisted of only two tanks in series, a reactor with a short holdup (5-10 minutes) followed by one with a long holdup (60-80 minutes). As shown by laboratory testing conducted after these runs, a long holdup CSTR does not produce good settling solids. In fact, as shown in the laboratory tests and the open-loop pilot plant runs, the solids properties deteriorate with increasing reaction time (batch or CSTR) either because of increased solids holdup or increased limestone conversion.

- Recirculation of poor solids -- The onset of recirculation of solids from the thickener overflow through the scrubber and back to the reactor system marked the beginning of deterioration of settling properties in the reactor system. Poor settling solids were already present, though in the thickener, apparently because it is like a poorly stirred CSTR with a 4-6 hour holdup

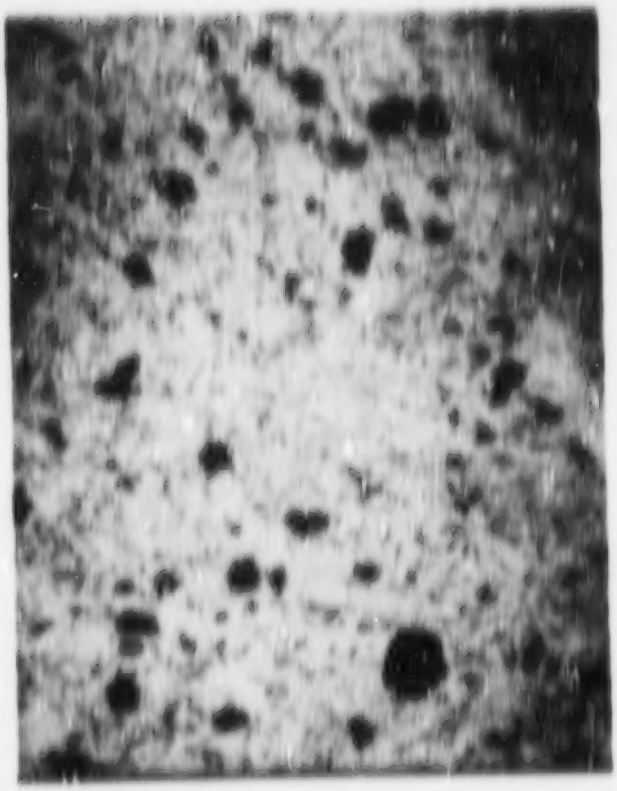


FIGURE VI-46 CRYSTALS IN REACTOR 4, 28 HRS INTO RUN USING LIMESTONE (RUN 430)

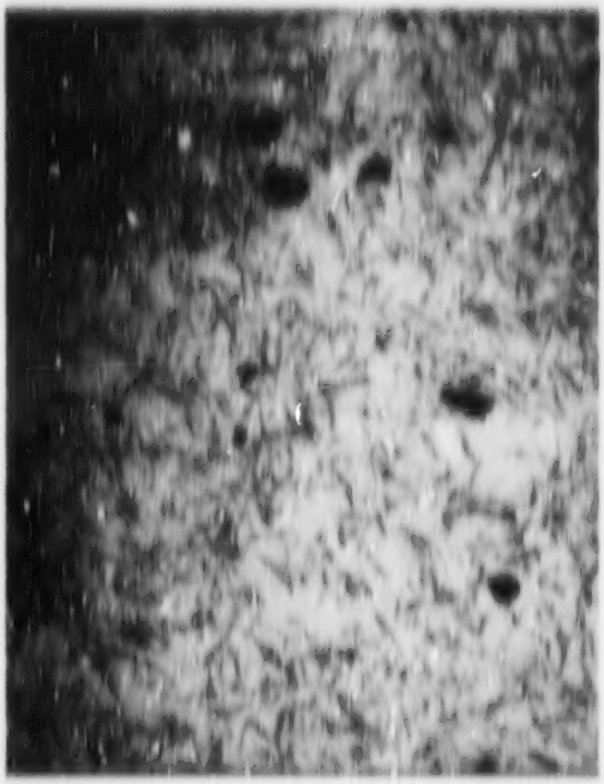


FIGURE VI-48 CRYSTALS IN REACTOR 4, 48 HRS INTO RUN USING LIMESTONE (RUN 430)

FIGURE VI-47 CRYSTALS IN REACTOR 3, AFTER 48 HRS OF RUNNING WITH LIME (RUN 430)

FIGURE VI-48 CRYSTALS IN REACTOR 3, AFTER 67 HRS OF RUNNING WITH LIME (RUN 430)

FIGURE VI-49 CRYSTALS IN REACTOR 3, 8 HRS AFTER RESUMING LIMESTONE FEED (RUN 430)

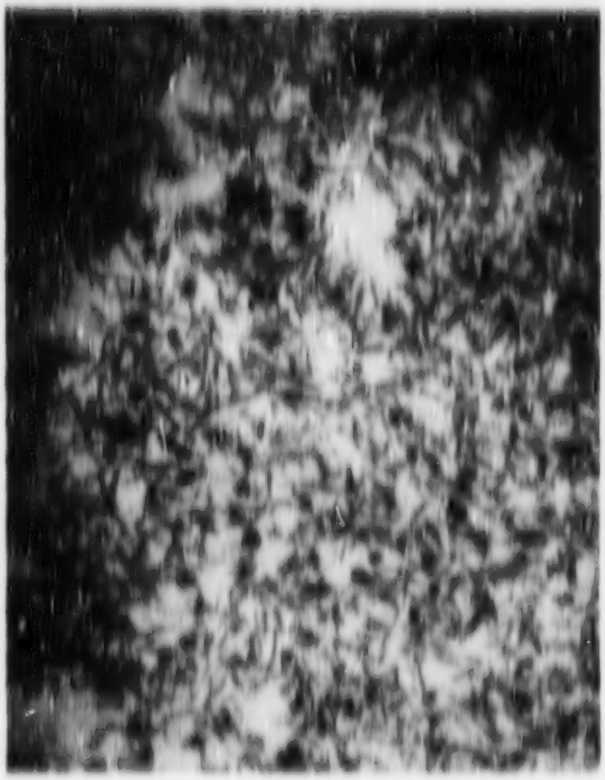


FIGURE VI-50 CRYSTALS IN REACTOR 3, 30 HRS AFTER RESUMING LIMESTONE FEED

in which a large fraction of the reaction was occurring. There was also precipitation of some calcium-sulfur salts in the scrubber under non-optimal conditions and possibly some re-dissolution at low pH's, both of which contributed to the poor quality of the solids feeding into the reactor system.

Figure VI-31 shows the difference in the settling properties of solids from reactors 1 and 3 just prior to and just after an appreciable quantity of solids began overflowing the thickener. This phenomenon occurred in all runs and thwarted attempts to reestablish good settling solids by draining and repriming the venturi recycle tank and reactors (but not the thickener).

In addition to adjusting reactor configuration and holdup, repriming tanks and using intermittent lime feed, four other methods were tried in an effort to improve solids settling properties:

- addition of fly ash to the first reactor (to speed CO_2 off-gassing);
- recycle of thickener underflow to the reactor system (to grow better crystals);
- use of flocculants (to increase settling rates); and
- adjusting operating pH and the limestone feed rate.

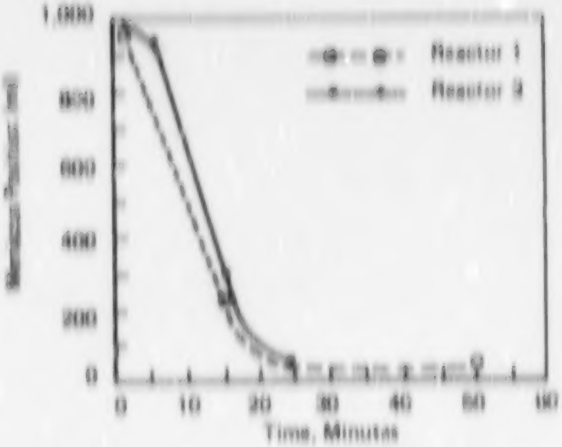
None of these proved successful. The flocculant did increase the settling rate, but the final settled volume did not change.

Based upon these results, additional work is required to develop an operable concentrated limestone mode.

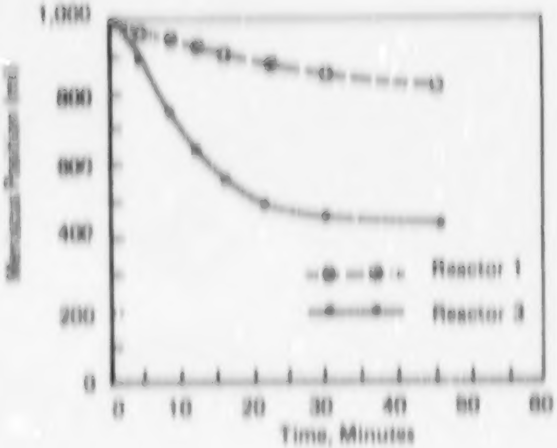
D. CONCLUSIONS

No viable approach was found for use of limestone in a concentrated dual alkali mode. Through the laboratory and pilot plant efforts allocated to work on the concentrated limestone mode, we were not able to develop process parameters and reactor conditions consistent with good limestone utilization and generation of acceptable quality waste solids. The work did, however, uncover important factors influencing the limestone regeneration reaction that indicated promising areas of future work. Unlike results from work on use of limestone in dilute modes (see Chapter VII), the potential for technical success argues for additional work on the concentrated limestone dual alkali mode; especially when the economic incentives (presented in the Introduction, Chapter II) are considered.

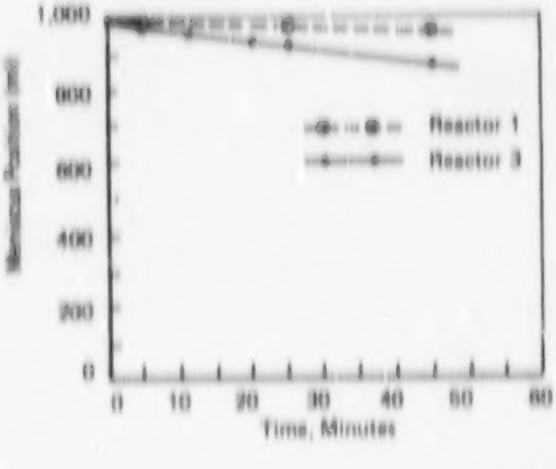
Limestone is substantially less reactive toward sodium salt solutions than is lime, even when reacting with relatively acidic scrubber bleed solutions. The reaction rate of the limestone regeneration reaction is dependent upon:



Settling Curves 1 Hr.
Before Noticeable Solids
In Overflow



Settling Curves 3 Hrs.
After Solids Carryover
From Thickener



Settling Curves 4 Hrs.
After Solids Carryover
From Thickener

FIGURE VI–61 SETTLING CURVES FOR RUN 430

- nature of the limestone and its particle size distribution;
- reactor temperature and residence time;
- concentrations of soluble reactants (sodium sulfites, sodium bisulfites and sodium sulfates); and
- the presence, at low concentrations, of trace constituents, such as magnesium and iron, which influence the reaction rate.

Increase in the reaction rate was generally consistent with improvement in the dewatering properties of the solids produced and with improved utilization of limestone.

Three limestones, with similar particle size distribution, were examined -- Fredonia limestone used in the EPA/TVA Shawnee program; another, locally available, natural limestone; and reagent grade $CaCO_3$. Of these, the Fredonia limestone was amorphous, rather than crystalline in nature, and was considerably more reactive than the other two limestones examined. The Fredonia limestone, therefore, was used extensively in the laboratory and pilot plant programs.

Laboratory experiments indicated that increasing temperature importantly increased the reaction rate. However, the pilot plant was not equipped for heating the reactors or for heating the reactor feed. As a consequence pilot plant regeneration was performed at a maximum of about 50°C.

The dewatering properties of solids were generally observed to deteriorate as the regeneration reactor residence time was increased. Increasing the reactor residence time results in carrying out the reaction closer to the equilibrium conditions and consequently at a lower driving force and reaction rate. Use of multistage reactor systems, containing several stages with residence times in the range of 15 minutes, were found to produce solids with a quality superior to that of solids produced in fewer reactors with the same total residence time. Recycle of solids, increasing reactor solids concentrations from about 2 wt % to 5 wt %, improved limestone utilization but did not appreciably improve the quality of the solids.

Under controlled conditions, with a multistage reactor system operating at about 50°C, it was possible to produce solids with acceptable dewatering properties (45% insoluble solids) and to achieve limestone utilizations on the order of 75%. However, as the sulfate concentration in the loop rose above 0.7M, or the magnesium concentration rose much above 100 ppm, the reaction rate and the resulting limestone utilization and solids properties all deteriorated.

Sulfate concentration in the reactor liquor had a much more important, deleterious effect on the reaction rate and solids properties in limestone regeneration reactions than the similar effects of increased sulfate concentration observed in concentrated lime regeneration. As in lime regeneration; the reaction rate is inversely proportional to the ratio of sulfate/sulfite concentrations in the liquor, but the rate drops dramatically using limestone as the sulfate concentration exceeds 0.7M at TOS levels of 0.3-0.5M. Operation at lower sulfate/sulfite ratios tends to limit sulfate precipitation in this mode and limit the range of oxidation in which limestone regeneration could be operated closed loop.

Calcium sulfate coprecipitates along with calcium sulfite in concentrated limestone regeneration reactions in an analogous fashion to the coprecipitation of calcium sulfate observed in the concentrated lime regeneration. However, pilot plant data indicate that for the same sulfate/sulfite concentrations with the same range of TOS in the feed liquor (i.e., [TOS] = 0.3-0.5M) lower sulfate precipitation occurs when using limestone, as given by the following:

$$\left(\frac{CaSO_4}{CaSO_3}\right)_{\text{reactor solids}} = 0.032 \left(\frac{[SO_4^=]}{[SO_3^=]}\right)_{\text{reactor liquor}} \qquad (3)$$

The sensitivity of the reaction to high sulfate concentrations and the lower sulfate precipitation rates make limestone regeneration less viable for closed-loop operation than lime regeneration at higher oxidation rates.

The presence of Mg^{++} in solution, introduced into the system in varying amounts depending upon the magnesium content of the limestone, also can have a retarding effect on the limestone regeneration reaction rate, resulting in poor solids quality and limestone utilization. This effect becomes pronounced as the Mg^{++} concentration rises much above a few hundred ppm. Relatively low magnesium limestones, such as Fredonia limestone (1.0-1.5 wt % Mg as $MgCO_3$), would result in concentrations on the order of a few thousand ppm, at steady-state, in a concentrated dual alkali loop.

Laboratory work confirmed that magnesium concentrations could be controlled by reacting part of the process stream with lime to precipitate $Mg(OH)_2$. However, such an approach would reduce operating cost savings, requiring part of the total regeneration to be performed using lime. Use of lime with limestone would increase the complexity and the capital cost in a manner similar to that discussed in Chapter VII for dilute limestone/lime dual alkali systems, eliminating economic incentive.

In pilot plant operations, iron from corrosion of unlined steel equipment was found to have an effect similar to that of magnesium on the limestone regeneration reaction at pH's below about 6. At higher pH's, $Fe(OH)_3$ is highly insoluble, limiting the buildup of iron in solution. By selection of proper materials of construction and linings and by carrying the limestone regeneration beyond a pH of 6, interference by iron can be eliminated in concentrated limestone modes.

Future work on limestone regeneration should be directed at increasing reaction rates at high magnesium levels by increasing sulfite concentrations, reactor temperature and by staging of the reactors.

VII. LIMESTONE/LIME DILUTE MODES

As explained in the introduction, operating with dilute sulfite/bisulfite (TOS) solutions represents one possibility for increasing the proportion of sulfate in the cakes produced during regeneration. Against this possible benefit must be balanced the cost penalties (represented by larger equipment and higher pumping rates) caused by operating with more dilute TOS solutions.

A. EPA LABORATORY RESULTS

In its Research Triangle Park laboratories, EPA had already performed some preliminary scouting runs on the regeneration of dilute TOS solutions with limestone and lime. These were summarized by Drehmel,[11] who showed that the $CaSO_3$ exhibited a pronounced tendency to supersaturate; i.e., the reactions:

$$CaCO_3 + 2NaHSO_3 \rightarrow CaSO_3(s) + Na_2SO_3 + CO_2\uparrow + H_2O \qquad (7)$$

$$Ca(OH)_2 + 2NaHSO_3 \rightarrow CaSO_3(s) + Na_2SO_3 + 2H_2O \qquad (8)$$

did not proceed rapidly to completion in dilute TOS solutions. The preliminary runs indicated that this tendency could be counteracted by recirculating the product solids through the reactor, and that maintaining a level of 5% solids in the reactor might permit reasonable utilization (80-90% with lime, 50-70% with limestone), with one-hour holdup times.

EPA extended this work by performing a series of continuous limestone runs in a 2-liter reactor followed by a 5-liter clarifier, with slurry recycle to the reactor. These were long-term runs (36-50 hours in length) at about 50°C. Satisfactory material balances were calculated for all, using an ADL computer program adapted for the purpose; this program performs balances around designated sections of the circuit for total weight, total volume, and the weight of water, sulfur, sulfate, sodium, and calcium.

The pertinent results for the 10 Fredonia limestone runs are summarized in Table VII-1. In all runs, a 17-20% $CaCO_3$ slurry was added to the TOS/SO_4 feed solution, with a one-hour residence time in the reactor and a two-hour residence time in the thickener. Solids recycle was maintained from the thickener to the reactor to achieve the suspended solids concentrations shown in the table.

The total sulfate content of the well washed samples of cake was determined and reported as $CaSO_4$. Attempts to increase the sulfate content of the cake by decreasing TOS and raising sulfate levels in solution met with only marginal success. Instead, this approach resulted in poor efficiency for TOS removal and poor Ca utilization. One interesting trend can be noted by observing the cake sulfate content in runs 21, 24, 25, and 27,

TABLE VIII-1

EPA 2-LITER REACTOR CONTINUOUS FREDONIA LIMESTONE RUNS—SUMMARY

Run	Feed Solution Composition, M [TOS]	Feed Solution Composition, M [SO$_4$]	Percent Solids in Reactor	Calcium Feed Stoichiometry	Calcium Utilization TOS Basis,[a] %	$\left(\frac{CaSO_3}{CaSO_4}\right)_{in\ Solids}$
21	0.14	0.25	2.1	1.13	90	10.18
22	0.14	0.52	2.2	1.78	66	8.5
23	0.14	0.41	2.9	1.19	73	6.8
24	0.13	0.26	4.6	1.02	116	6.1
25	0.13	0.26	6.0	1.25	106	8.2
26	0.04	0.25	2.7	0.88	133	6.3
27	0.12	0.27	3.5	1.25	78	4.5
28	0.07	0.27	3.3	0.78	110	11.1
29	0.05	0.53	2.8	0.72	55	22.2
30	0.04	0.73	2.8	0.84	52	8.2

a. 100 x mols TOS Removed/mol Calcium Added all conducted with essentially the same feeds and the same nominal stoichiometry, but differing in percent solids level in the reactor. There appears to be a downward trend in cake sulfate level as percent solids level (and thus effective solids residence time) in the reactor is increased.

On the other hand, lowering the TOS and raising the sulfate levels in solution did render a lime post-treatment more effective in precipitating sulfate from solution. In runs 26 through 30, samples of the thickener overflow were agitated with excess lime for one hour, and the sulfate disappearance from solution was monitored. Table VII-2 shows the results for these runs, in terms of the ability of the system to reject sulfate as a fraction of total sulfur species precipitated, both for the lime step only and for the combination of the limestone and lime step (assuming all limestone step overflow to go on to lime treatment). The lime treatment solids in runs 29 and 30 were analyzed and, as the table shows, the check with sulfate precipitation from solution is quite good.

The calcium and sulfate levels in the limestone reactor overflow and thickener underflow solutions of runs 26 through 30 were multiplied for comparison with the apparent molal solubility product for $CaSO_4 \cdot 2H_2O$ (predicted by the method of Kusik and Meissner[7]) for the ionic strength involved. Figure VII-1 shows that in all runs (runs 21 through 30) levels were not high enough to precipitate $CaSO_4 \cdot 2H_2O$ as such; however, whenever crystals of $CaSO_4 \cdot 2H_2O$ were shaken with samples to test for calcium sulfate saturation, the product of the calcium and sulfate levels in the resulting solution rose to the predicted curve almost exactly (the squares on Figure VII-1). Figure VII-2 shows similar calculations for the calcium times the sulfite, compared with the analogous curve for $CaSO_3 \cdot 1/2H_2O$. In all runs, $CaSO_3$ supersaturation is indicated.

B. DILUTE MODE ALTERNATIVES

The results of this work have been utilized to help us project possible flow sheets for dilute operation at 35% sulfate precipitation rates. We have compared

- using limestone, with lime for added sulfate precipitation, and

- using lime, with sodium carbonate for added Ca softening.

The first of these has been called the "double loop-sulfite softening" mode because the calcium level leaving the lime reactor/clarifier is lowered by recycling the solution to the limestone reactor, in which the precipitation of $CaSO_3$ lowers the Ca level.

Figure VII-3 shows how one would operate a dilute limestone/lime system to precipitate sulfate to sustain a 35% oxidation level, based on the results of EPA run 30. About one-quarter volume of regenerated liquor would have to be sent to a lime loop (for sulfate precipitation) for

TABLE VII-2

EPA RUNS - POTENTIAL OF LIME POST-TREATMENT STEP

	Concentrations in Feed Liquor, M		Concentrations in Treated Liquor, M		$\left[\frac{\Delta SO_3^=}{\Delta(SO_3^= + TOS)}\right]_{liquor}$	$\left(\frac{CaSO_4}{CaSO_x}\right)_{solids}$
	$[SO_3^=]$	[TOS]	$[SO_3^=]$	[TOS]		
LIME STEP ONLY						
Run 26	0.2721	0.0234	0.2925	0.0090	(0)	-
27	0.2845	0.0648	0.2886	0.0180	(0)	-
28	0.2511	0.0418	0.2523	0.0214	(0)	-
29	0.5349	0.0326	0.5125	0.0100	49.8%	41.9%
30	0.7389	0.0313	0.6999	0.0106	65.3	84.5
LIMESTONE PLUS LIME OVERALL						
Run 26	0.2420[a]	0.0292[a]	0.2925	0.0090	(0)	-
27	0.2860	0.1183	0.2886	0.0180	(0)	-
28	0.2626	0.0712	0.2523	0.0214	17.2%	-
29	0.5298	0.0443	0.5125	0.0100	29.5	-
30	0.7183	0.0401	0.6999	0.0106	38.4	-

a. These (and following) adjusted for dilution of feed with limestone slurry.

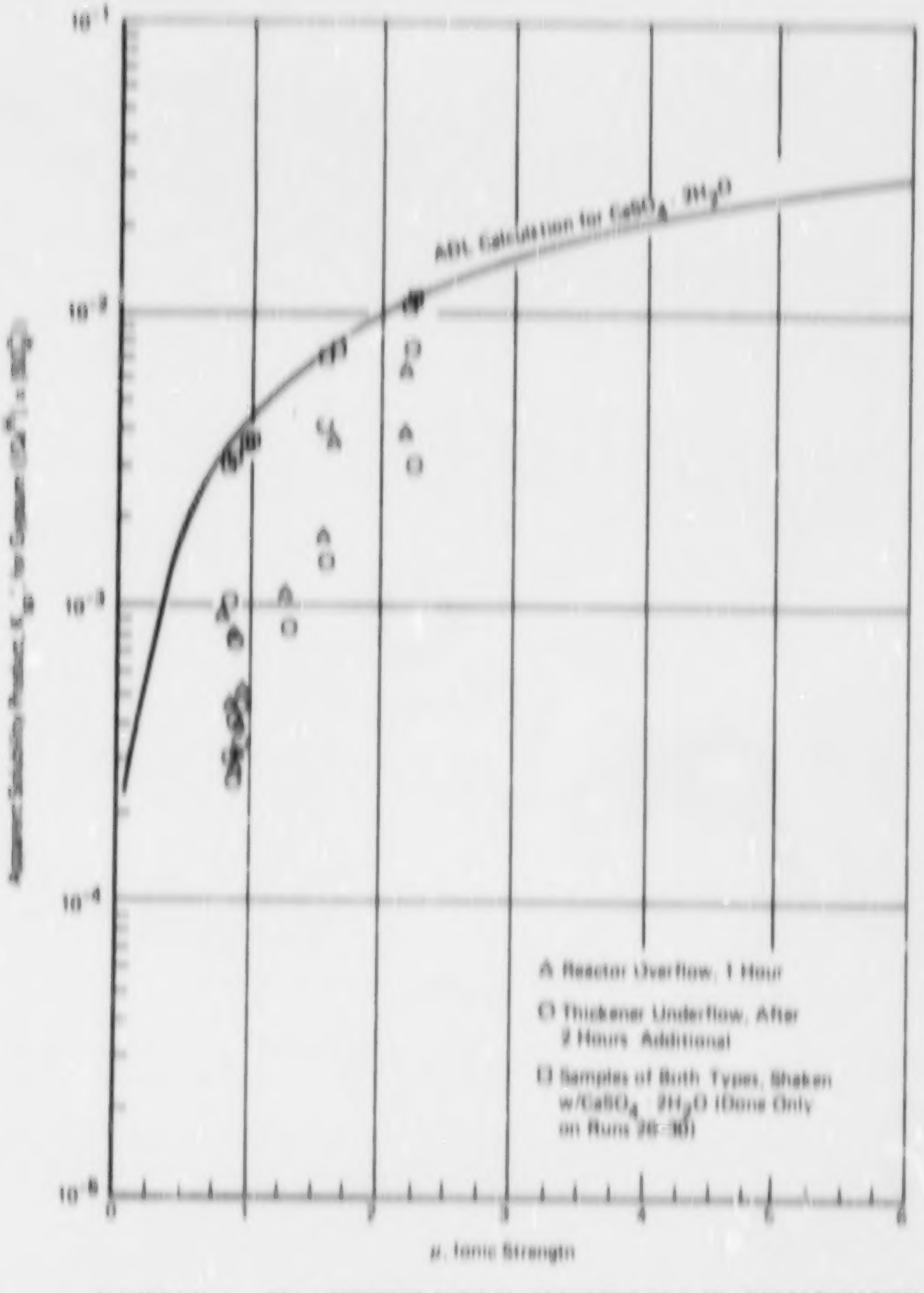


FIGURE VII–1 EPA LIMESTONE RUNS 21–30 EXTENT OF $CaSO_4$ SUBSATURATION

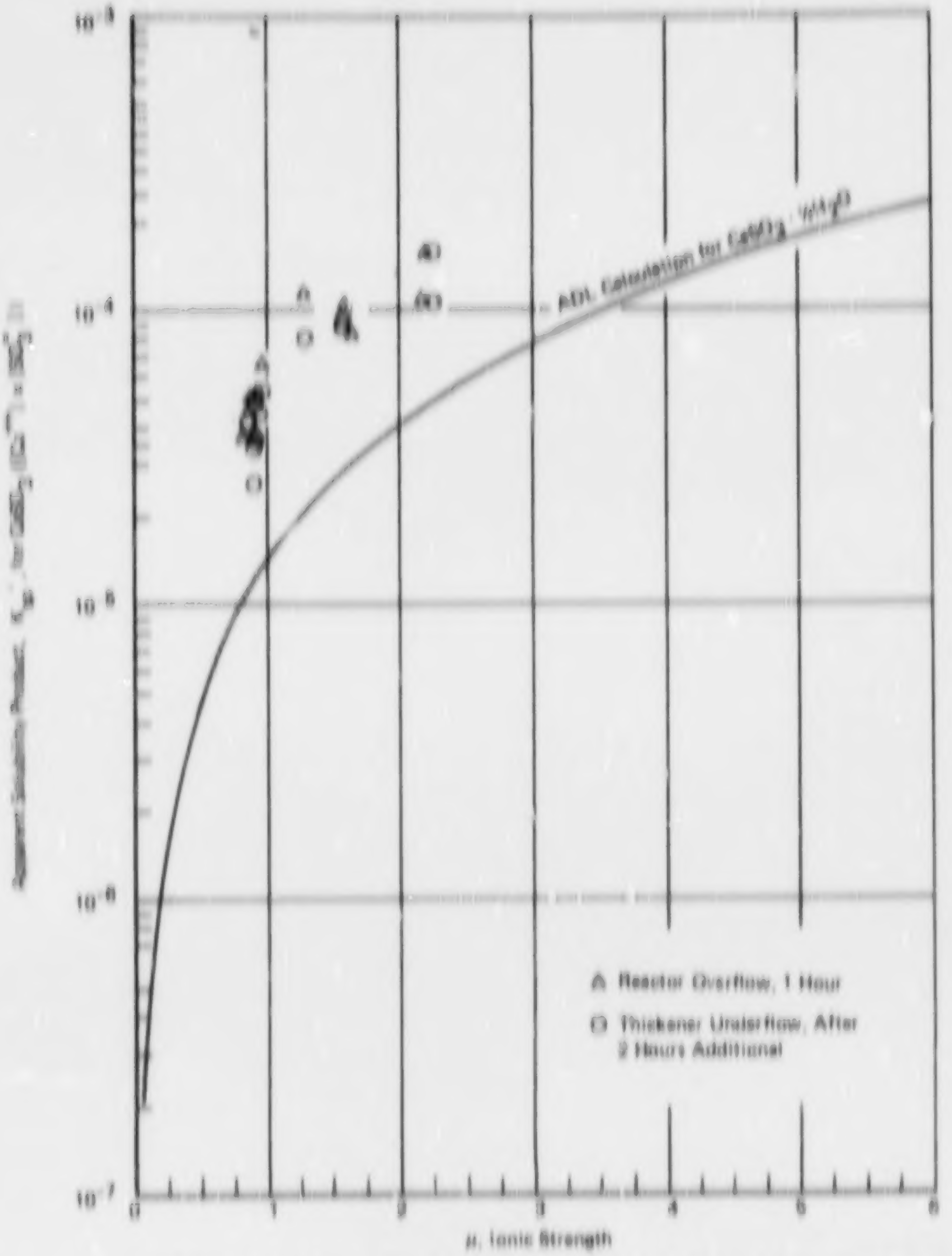
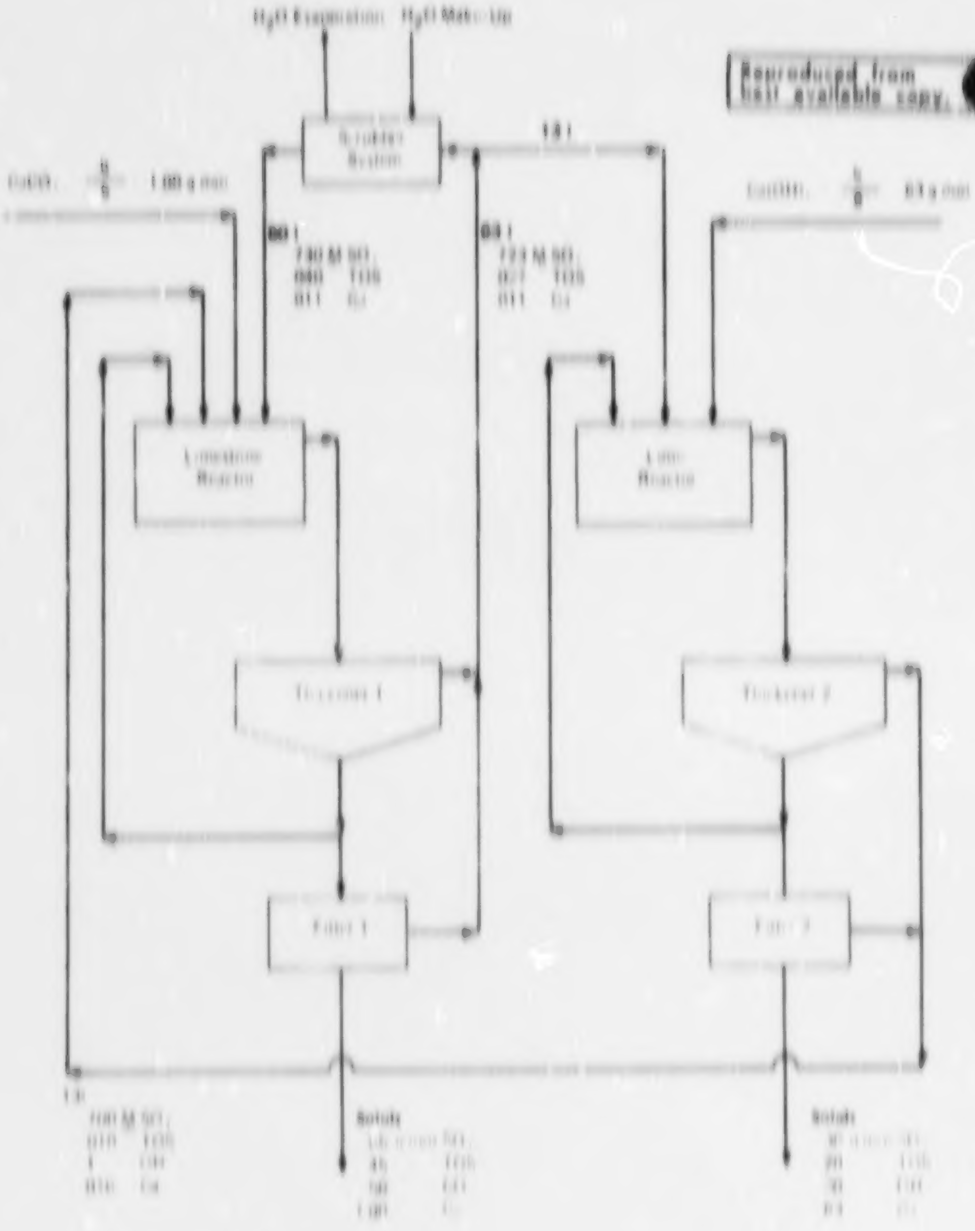


FIGURE VII-2 EPA LIMESTONE RUNS 21–30 EXTENT OF Ca SO_3 SUPERSATURATION

Reproduced from best available copy.


H_2O Evaporation
H_2O Make-Up
Scrubber System
181
801
.730 M SO_3
.060 TDS
.011 Cl
681
.723 M SO_3
.027 TDS
.011 Cl
1.00 g mol
.63 g mol
Limestone Reactor
Lime Reactor
Thickener 1
Thickener 2
Filter 1
Filter 2
Solids
Solids

Basis: 1 g mole of SO_2 absorbed
[illegible]

FIGURE VII-3 DILUTE LIMESTONE/LIME SCHEMATIC

every volume sent to the scrubber. At these conditions, the material returned to the scrubber would be undersaturated (with respect to $CaSO_4 \cdot 2H_2O$) by about 150 ppm Ca. The expected utilizations are only 50% for limestone and 80% for lime, based on experimental results. If one tries to keep up with higher levels of oxidation by sending higher fractions through the lime loop, the calcium undersaturation ("safety factor") decreases as the material leaving the lime reactor, which is saturated in $CaSO_4 \cdot 2H_2O$, begins to overpower the sulfite softening occurring in the limestone reactor; indeed, it does not appear possible to keep up with more than 40% oxidation without having to accept a regenerated scrubber liquor with a calcium level approaching within less than 100 ppm Ca of saturation with respect to gypsum.

Figure VII-4 shows how one might operate an alternative flow sheet using lime only, relying on sodium makeup with Na_2CO_3 for the necessary Ca softening. Again a 35% oxidation level has been taken as a basis. The expected $Ca(OH)_2$ utilization is about 80%. The amount of sodium in the Na_2CO_3 needed for softening to a level 100 ppm below saturation is seen from Figure VII-4 to be less than 1% of the weight of the dry waste solids. Since soluble Na losses in well washed cakes have been in the range of about 1%, the normal makeup of Na should introduce more than enough carbonate for softening.

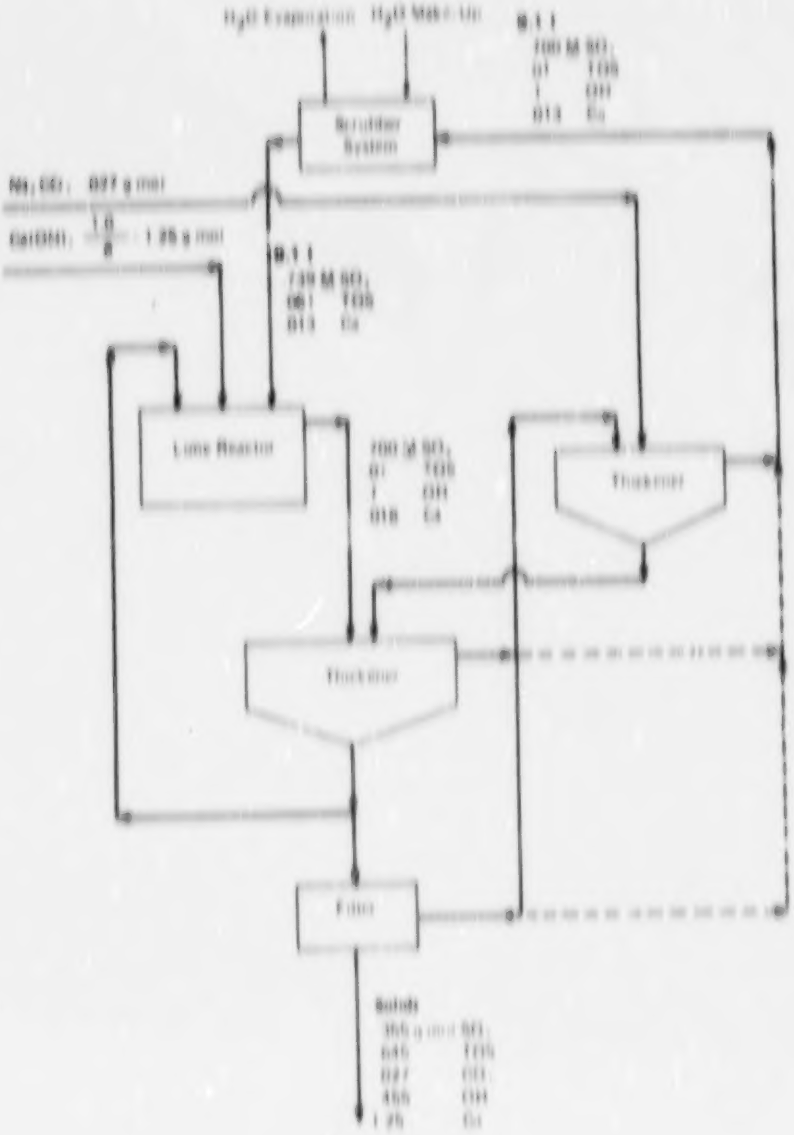
The mode of operation in Figure VII-4 has a much smaller scrubber liquor feed; while the mode of Figure VII-3 requires 50 l/g mol SO_2 absorbed, that of Figure VII-4 requires 9.1 l/g mol SO_2 absorbed. The chief uncertainties in the mode of Figure VII-4 are:

1) amount of solids recycle required to produce good settling and to eliminate $CaSO_4$ supersaturation in the lime reactor,

2) ability to produce good-settling carbonate solids in the carbonate treatment thickener, and

3) ability to bypass some liquor around the carbonate treatment step to save on the cost of the thickener (see dashed lines in Figure VII-4).

Based upon the schematic process flow sheets developed from the laboratory data, rough economic analyses were made comparing the two dilute systems: limestone/lime with sulfite softening and lime with soda ash softening. The limestone/lime system involves higher capital costs because of the higher flow rates through the absorption/regeneration system, but it has lower raw material costs since half of the regeneration is carried out using limestone, as opposed to complete regeneration using the more expensive lime in the alternate dilute system. It was assumed that both systems would have the same effective cake washing efficiency and require approximately the same sodium makeup. Because of lower yields on raw materials, the limestone/lime system generates more waste for disposal.


H$_2$O Evaporation
H$_2$O Make Up
Scrubber System
Na$_2$CO$_3$: .027 g mol
Ca(OH)$_2$: $\frac{1.0}{.8}$ = 1.25 g mol
Lime Reactor
Thickener
Thickener
Filter
Solids
.355 g mol SO$_3$
.645 TOS
.027 CO$_3$
.455 OH
1.25 Ca

Basis: 1 g mol of SO$_2$ absorbed
[illegible] Oxidation Rate (all assumed in scrubber for convenience)

FIGURE VII-4 DILUTE LIME/CARBONATE SOFTENING SCHEMATIC

On the basis of the following analysis, it was found that the raw material cost savings for the limestone/lime system were not sufficient to offset the expected capital cost increases and increases in waste disposal costs.

Two cases were examined for the economic analysis:

- a 3.5% S coal application requiring 90% SO_2 removal, and
- a 1.0% S coal application requiring 80% SO_2 removal.

In both cases a relatively large cost difference was assumed between lime and limestone:

- $40/ton, CaO (80% utilization)
- $5/ton, $CaCO_3$ (ground, 50% utilization)

This large cost difference in materials favors the more capital-intensive sulfite softening approach. A waste disposal cost of

- $10/ton waste (dry basis)

was used in all cases. A total annual fixed cost of 20% of the capital investment (including maintenance costs) was used to calculate annual costs.

Using this basis, we calculated the minimum capital investment difference at which the annual capital cost savings of the simpler lime approach equaled the annual operating cost savings of the limestone/lime approach. For the high-sulfur coal case, a capital investment savings of about $7/kw or more would offset operating cost savings. In the low-sulfur coal situation, the corresponding figure dropped to only $1.8/kw. In each case, we would expect the actual capital investments for the limestone/lime system to easily exceed those of the lime system by more than these calculated values. As a result, lime regeneration with soda ash softening was selected as the basic approach to be investigated for dilute modes in future pilot operations under this program.

C. ADL LABORATORY STUDIES

The results obtained during the EPA laboratory research program showed that if a lime or soda ash softening step were included, limestone could be used to perform some of the regeneration in dual alkali FGD systems operating at dilute active sodium concentrations. However, because it was estimated that the capital costs associated with a dual reagent (limestone/lime) system would be substantially higher as compared to a system using only lime, the remaining studies of dilute mode systems at ADL were focused on the latter.

The several unit operations which would comprise dilute mode schemes were first studied in a matrix of open-loop tests in the ADL pilot plant. The individual unit operations were then to be assembled and subjected to extended closed-loop testing. During the open-loop tests in the pilot plant, unexpectedly high effluent soluble calcium levels were observed in some of the runs. Saturation tests indicated that the solutions were supersaturated with respect to calcium sulfate (gypsum). In an attempt to better understand the phenomena responsible for calcium supersaturation, a program of laboratory experiments was undertaken in parallel with the studies being performed in the pilot plant.

Initially, a series of experiments was carried out in a laboratory scale continuous stirred tank reactor (CSTR). Batch experiments were then carried out, in which the rates of decrease of soluble calcium concentrations in the presence of different amounts and types of suspended solids were monitored. Measurements of the equilibrium solubility of gypsum at various sodium sulfate concentrations, hydroxide concentrations, and temperatures were also performed to obtain fundamental data against which to compare experimental observations.

1. Studies of Calcium Precipitation from CSTR Effluents

The effect of total oxidizable sulfur (TOS) concentration on the composition of the regenerated solution was studied at 50°C in a 1-liter CSTR operating at a residence time of 30 minutes. The pH of the feed solution was maintained in the range of 5.4-5.6 in all cases and 300 ppm calcium was added to the feed solution to simulate a dilute mode scrubber bleed stream. The lime feed was adjusted so that the amount fed was 110% of the amount theoretically required to produce 0.12M hydroxide in the reactor effluent.

The results obtained from three CSTR experiments in which TOS levels (after dilution by the lime slurry) were about 0.041M, 0.023M, and 0.00M are shown in Table VII-3. In all cases, the concentration of hydroxide in the effluent reached only about 0.1M, indicating that a significant portion of the lime had not reacted. For the intermediate TOS level, the effluent hydroxide concentration was about 10% less than that observed in the other two experiments. In both experiment 47 and experiment 50, the concentration of TOS in the reactor effluent was about 0.02M, approaching the sulfite saturation level for these solutions. The solids from experiment 47, in which a very small reduction in soluble TOS was observed, contained only 6% of the calcium/sulfur salts as calcium sulfite.

In all three cases, the reactor effluent solutions were supersaturated with respect to gypsum. With TOS present in the feed, soluble calcium levels were higher than in experiment 48 where no TOS was fed. Equilibrium saturation levels of calcium with respect to gypsum at 20°C, as determined by equilibrating the supernatant liquid with excess gypsum crystals, were essentially the same for all three experiments. The same test, but carried out at the reaction temperature of 50°C, indicated that gypsum solubility was greater at that higher temperature. Consequently, conducting the saturation test at a temperature lower than the reaction temperature produced results which would indicate a greater degree of supersaturation than actually existed under reactor conditions.

TABLE VII-3

DILUTE MODE CSTR EXPERIMENTS[a]

Feed Solution	Expt. 50	Expt. 67	Expt. 68
[TOS], (M)	.0407	.0237	0.0
$[Ca^{++}]$, (M)	.0075	.0015	.0075
$[SO_4^=]$, (M)	.557	.506	.517
Reactor Effluent Solution			
[TOS], (M)	.0203	.0220	0.0
$[Ca^{++}]$, (M)	.0265	.0275	.0230
$[Ca^{++}]$, Gypsum Saturation, (M)	.0164 (20°C)	.0168 (20°C) .0183 (50°C)	.0157 (20°C) .0170 (50°C)
$[SO_4^=]$, (M)	.486	.458	.478
$[OH^-]$, (M)	.106	.097	.107
Reactor Solids			
Mol % $CaSO_4/CaSO_x$	43.4	94.0	100.0

---

[a] CSTR residence time, 30 mins.; temperature, 50°C; feed solution pH, 5.4-5.6; limestone feed stoichiometry, 110% of amount required to produce 0.12M hydroxide.

In an attempt to gain insight into the effect of various combinations of reactor residence time and suspended solids concentrations on effluent soluble calcium levels, a series of batch experiments was conducted in which portions of effluent slurry from the CSTR were allowed to react for additional periods of two hours in the presence of varying amounts of added suspended solids. Experiment 4B (no TDS) was repeated and the CSTR was operated for a time sufficient to allow a quantity of reaction solids to be produced and collected. After the solids were collected, CSTR operation was continued and portions of the effluent slurry were taken directly from the reactor overflow and placed in stirred flasks held at 50°C. Quantities of additional solids (either reactor product solids or reagent grade gypsum crystals) were added to the flasks immediately after the slurry was collected from the CSTR. Samples of slurry were then taken from the stirred flasks and analyzed at intervals throughout the two-hour reaction period. The results from this set of experiments are shown in Table VII-4. The weight percent solids listed in Table VII-4 are the total suspended solids which were present in each flask, i.e., including the 0.5 weight percent solids initially present in the reactor slurry itself.

For the sample which had no additional solids added, the calcium concentration decreased to essentially the saturation value of 0.017M after sixty minutes. With a total of 3% solids present during the batch reaction, the soluble calcium levels after two hours were close to the saturation value with either reactor solids or gypsum added. However, the rate at which the calcium level fell was markedly greater in the case when the additional 2.5% solids were reagent-grade gypsum. With 6% total suspended reactor solids, the soluble calcium levels remained essentially constant for the duration of the two-hour experiment, but in the case where the added solids were gypsum, the levels were uniformly lower--essentially at saturation. With 9% reactor solids, the soluble calcium level again remained constant and was essentially the same as the level with 6% reactor solids.

The reason for the apparently faster equilibration, but to a higher final calcium level at 6% and 9% reactor solids, was not immediately obvious -- particularly when that behavior was contrasted to the behavior observed when gypsum was added. In the latter case, the equilibrium calcium level appeared to be independent of the total suspended solids concentration. One possible explanation was that since the reactor solids contained unreacted lime, adding further reactor solids resulted in a larger amount of unreacted lime, which led to the higher calcium levels. The results of the experiments do suggest, however, that under the conditions studied, additional reaction time may be as effective, or even more effective, in lowering the effluent soluble calcium level than recycling reaction solids.

2. Measurements of Gypsum Solubility

Since the gypsum solubility was observed to increase with temperature in the CSTR saturation tests and since there was a possibility that hydroxide concentration could also affect gypsum solubility, a series

TABLE VII-4

STUDY OF CALCIUM DE-SUPERSATURATION IN POST-CSTR BATCH REACTIONS[a]

Time After Slurry Removed from Reactor (mins.)	No Additional Solids (0.5%)		3% Total Solids				6% Total Solids				9% Total Solids	
			Reactor Solids		Gypsum		Reactor Solids		Gypsum		Reactor Solids	
	Ca^{++} (M)	OH^- (N)	Ca^{++} (M)	OH^- (N)	Ca^{++} (M)	OH^- (N)	Ca^{++} (M)	OH^- (N)	Ca^{++} (M)	OH^- (N)	Ca^{++} (M)	OH^- (N)
15	.0205	—	.0201	—	.0220	—	.0194	—	.0174	—	.0190	—
30	.0180	.112	.0198	.112	.0176	.115	.0191	.118	.0179	.125	[.0221][b]	.125
60	.0186	—	.0189	—	.0181	—	.0188	—	.0169	—	.0190	—
120	.0176	—	.0178	—	.0176	.115	.0191	.115	.0173	—	.0194	.122

---

[a] Reactor solids and slurries obtained from repeat of CSTR experiment 48.
Conditions: 50°C, 30 mins. residence, TDS = 1, $SO_4^=$ = 1.5, stoichiometry = 110% of lime required for 0.12N OH^-.
Reactor effluent solution: Ca^{++} = .0210M, Ca^{++} gypsum saturation = 0.0170M, OH^- = .112N

[b] Doubtful value.

of measurements of soluble calcium levels as a function of sodium sulfate concentration, hydroxide concentration, and temperature were made for solutions equilibrated in contact with excess solid gypsum.

The experiments were carried out by adding excess (about 5 g/100 ml solution) reagent grade $CaSO_4 \cdot 2H_2O$ to sodium sulfate/hydroxide solutions at room temperature. The mixtures were stirred, brought to temperature, and stirred at temperature for one-half hour. The solids were then allowed to settle for one-half hour at temperature, and finally a portion of the supernate was removed and centrifuged using temperature equilibrated glassware. The calcium and sulfate concentrations in the centrates were determined by the usual titrimetric methods.

The results of this series of measurements are shown in Table VII-5. In addition to a general increase in calcium concentration with an increase in temperature from 20°C to 55°C, a significant increase in soluble calcium was observed when the concentration of hydroxide was increased from 0-0.1M to 0.15M. The 0.017M concentration of calcium measured in experiments G and H at 55°C corresponds quite closely to the equilibrium levels observed in the batch and CSTR experiments described above. The fact that the concentration of hydroxide needed to be raised to 0.15M to achieve a soluble calcium level of 0.019M in these solubility experiments suggests that the 0.019M level observed in the earlier experiments (where hydroxide concentration was never greater than 0.125M) was probably due, in part, to the presence of unreacted lime.

These results show that erroneously high gypsum supersaturation can be indicated if solutions are allowed to cool before gypsum crystals are introduced for determination of saturation levels.

3. Additional Batch Reaction Studies of Dilute Mode Regeneration with Lime

To explore further the possibility that unreacted lime might have been responsible for the elevated calcium levels observed in some of the experiments described earlier, two batch reactions were carried out in which 0.5M Na_2SO_4 solutions were reacted with different amounts of lime. In one experiment (80% stoichiometric), the amount of lime added was 80% of that which would have been required to produce 0.12M hydroxide in solution. In the other, 130% of the amount of lime required to regenerate to 0.12M hydroxide was added. The measured levels of soluble calcium and hydroxide as a function of time in these experiments are shown in Table VII-6. For the experiment at 80% of stoichiometric, the soluble calcium level had approached the saturation value of 0.0165M after about 45 minutes. In the other experiment where excess lime was added, the soluble calcium level was higher and remained essentially constant throughout the experiment. The 0.019M level observed was essentially the same as the level observed in the previous batch experiments carried out with 6% and 9% reactor solids, suggesting that excess lime may have produced the higher calcium levels.

TABLE VII-5

SOLUBILITY OF CALCIUM SULFATE IN SODIUM SULFATE/HYDROXIDE SOLUTIONS

Expt. Series	Sodium Salt Species (Mol Per Liter) Na_2SO_4[a]	Sodium Salt Species (Mol Per Liter) NaOH	Soluble Calcium - Mol Per Liter at Noted Temperature <15°C	20°C	40°C	55°C	70°C
A	0.267	0	—	0.0113	0.0117	0.0120	(0.0160)[b]
D	0.267	0	0.0102	—	0.0118	0.0118	0.0113
B	0.506	0	—	0.0128	0.0140	0.0143	0.0147
I	0.535	0	0.0126	—	0.0130	0.0136	0.0140
E	0.509	0	—	0.0125	0.0129	(0.0124)[b]	0.0141
C	0.988	0	—	0.0155	0.0163	—— lost ——	
F	1.04	0	0.0160	—	0.0164	0.0172	0.0177
G	0.536	0.100	0.0150	—	0.0154	0.0171	(0.0160)[b]
H	0.527	0.100	—	0.0144	0.0160	0.0169	0.0185
J	0.526	0.150	—	0.0156	0.0173	0.0191	0.0190

---

[a] The sulfate values noted are the average for the experimental series; a separate sulfate measurement was made for each calcium measurement.

[b] Values in parentheses are thought to be erroneous.

TABLE VII-6

BATCH REACTIONS OF LIME WITH SODIUM SULFATE SOLUTIONS AT TWO STOICHIOMETRIES[a,b]

Time After Addn. (mins.)	80% Stoichiometry			100% Stoichiometry	
	Ca^{++} (M)	Ca^{++} Gypsum Saturation(M) @ 50°C	OH^-(M)	Ca^{++} (M)	OH^-(M)
15	.0200	.0160	.092	.0193	.120
30	.0182	.0175	.0935	.0194	.120
45	.0176	.0157	.094	.0197	.122
60	.0170	.0176	.094	.0190	.122
90	.0168	.0152	.095	.0187	.124
120	.0160	.0168	.095	.0190	.124
		Average .0165			

---

[a] 100% stoichiometry defined as amount of lime required to produce 0.120 OH^- in solution.

[b] Temperature, 50°C; $[Na_2SO_4]$, 0.5M.

Several additional batch experiments were carried out to investigate the kinetics of the regeneration of dilute mode liquors with TOS concentrations in the range of 0.02M to 0.05M. Regeneration behavior in that region of TOS concentration was of interest because it represented a region of transition between: the regeneration of solutions containing very little or no TOS (produced by intentionally oxidizing scrubber effluent prior to regeneration) in which the solid product is very nearly pure gypsum, and the regeneration of solutions containing higher levels of TOS in which no distinct gypsum phase can be observed in the product solids.

The results obtained when solutions containing 0.025M TOS and 0.047M TOS were regenerated with lime in batch reactions at 50°C are shown in Table VII-7. Included for reference from Table VII-6 are the results of the experiment in which no TOS was present. In all cases, the amount of lime was 130% of the amount which would have been required to produce 0.12M free hydroxide in solution. The concentration of sodium sulfate was 0.5M, and when TOS was present, the ratio of bisulfite:sulfite was 9:1.

Three distinctly different types of behavior were observed in the three experiments. When no TOS was present, the reaction was very nearly complete after 15 minutes. With 0.025M TOS present, the concentrations of calcium, hydroxide, and TOS in solution remained essentially constant for samples taken between 5 minutes and 30 minutes after the start of the experiment, indicating that no reaction was taking place. After that apparent induction period, the reaction proceeded during the interval between 45 minutes and 90 minutes with a resultant increase in OH^- concentration. However, the concentration of TOS continued to remain essentially constant, and the solid reaction product must have been primarily gypsum. Whether the apparent decrease in TOS during the first 5 minutes of reaction was real or due to experimental error is difficult to ascertain because the starting solution, which was prepared with known weights of reagents, was not analyzed before the lime was added. The reduction in acidity after 5 minutes of reaction was greater than the observed increase in calcium concentration, suggesting that some calcium sulfite might have been precipitated.

In the third experiment, the initial TOS concentration of 0.047M was confirmed by analysis before lime was added. A substantial decrease in TOS occurred during the first 5 minutes of reaction, and TOS was observed to continue to decrease throughout the experiment reaching 0.011M after 180 minutes -- well below the final TOS level in the preceding experiment, and below the saturation level for TOS in this solution. This possibly may be due to coprecipitation of calcium sulfite with calcium sulfate in a manner analogous to the coprecipitation of sulfate with calcium sulfite in concentrated dual alkali modes.

TABLE VII-7

BATCH REACTOR STUDIES OF THE EFFECT OF THE LEVEL IN REGENERATION WITH LIME[a]

Time (min.)	Initial [$SO_4^=$] = 0		Initial [$SO_4^=$] = 0.0259				Initial [$SO_4^=$] = 0.0629			
	[Ca^{++}], M	[OH^-], M	[Ca^{++}], M	[OH^-], M	[$SO_4^=$], M	[Ca^{++}]$_{sat'd}$, M[d]	[Ca^{++}], M	[OH^-], M	[$SO_4^=$], M	[Ca^{++}]$_{sat'd}$, M[d]
0	0.0	nil	0.0	(0.0225)[b,c]	0.025[c]	—	0.0	(0.0421)[b]	0.057	—
5	—	—	0.0475	1.0960	0.0258	0.0363	0.2630	0.0904	0.029	0.0263
10	—	—	0.0455	0.0880	0.0166	0.0266	0.0340	0.0980	0.022	0.0271
15	0.0293	0.120	0.0475	0.0890	0.0160	0.0266	0.0545	0.1010	0.020	0.0260
30	0.0196	0.120	0.0475	0.7885	0.0187	0.0266	0.0340	0.1022	0.017	0.0265
45	0.0197	0.122	0.0340	0.1025	0.0299	0.0277	0.0325	0.1022	0.017	0.0263
60	0.0190	0.122	0.0250	0.1175	0.0185	0.0273	0.0313	0.1040	0.013	0.0266
90	0.0187	0.124	0.0213	0.1230	0.0182	0.0275	0.0271	0.1110	0.012	0.0269
120	0.0190	0.124	0.0200	0.1230	0.0186	0.0275	0.0250	0.1129	0.012	0.0274
180	—	—	—	—	—	—	0.0223	0.1192	0.011	0.0277

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[a] Temperature, 50°C; [Na_2SO_4], 0.5M; lime feed, 150% of amount required to produce 0.12M free hydroxide.

[b] Acidity equivalent to [HSO_4^-].

[c] Based on weighed reagents, not analyzed.

[d] Soluble calcium concentration after equilibrating reagents with excess gypsum at 50°C.

D. PILOT PLANT OPERATIONS

1. Introduction

As discussed previously, operation of dual alkali systems at dilute active sodium concentrations offers one possibility for increasing the proportion of calcium sulfate in the waste cake. Dilute dual alkali modes are defined as those in which the reactor solutions are saturated with respect to calcium sulfate. Under normal operating conditions this occurs with active sodium concentrations roughly equal to or less than 0.15M Na^+.

There are two basic approaches to operating in the dilute mode using lime for regeneration. One approach is to oxidize the scrubber effluent liquor intentionally to convert all the sulfite and bisulfite to sulfate prior to regeneration. The resulting waste solids, therefore, are calcium sulfate, usually in the form of gypsum, with no calcium sulfite. The second approach is simply to regenerate the scrubber bleed liquor directly, without oxidation. The waste cake is then a mixture of calcium sulfite and sulfate with the ratio of the two salts dependent upon the rate of oxidation in the scrubber system and the concentrations of sodium salts in the liquor. The calcium sulfate can be produced as a dihydrate (gypsum) or hemihydrate mixed with sulfite, or both, depending upon the system conditions.

Both of these approaches were included in the evaluation of dilute modes in the pilot plant. Testing was performed in two phases. The first phase consisted of batch and continuous open-loop runs of specific unit operations in the regeneration system. These included tests of the absorbent regeneration reactor, the carbonate softening reactor, and an aeration system for oxidation of the scrubber bleed liquor. Emphasis in this phase of testing was placed on the regeneration reactor. Runs were geared toward characterizing reactor performance over a range of conditions in order to develop suitable design and operating parameters. Testing of the oxidation of scrubber bleed liquor and carbonate softening was included primarily to ensure that no major difficulties would be encountered in implementing these operations in the pilot plant system. For the most part, the softening and oxidation operations were straightforward and not considered to present undue problems in full-scale systems.

The second phase of testing consisted of a number of closed-loop runs combining gas scrubbing, absorbent regeneration, and waste solids separation and dewatering. The object of these runs was to confirm the open-loop results; to optimize and characterize, to the extent possible, the performance of the integrated dilute mode operation; and to identify major problem areas or limitations of dilute mode operations. The runs lasted from a few days to up to a few weeks, depending both on the type of data required and the success of the system operation.

Throughout all of this work, hydrated lime was used for regeneration. The hydrated lime was metered to the reactor system as a dry solid

(90% through 200 mesh). On the average, the lime contained approximately 87% available calcium as calcium hydroxide. The hydroxide content of different batches of lime, though, ranged from 80% to 92%.

2. Reactor System Characterization (Open-Loop Operation)

As in the testing of the concentrated lime mode, the characterization of the reactor system operation was based upon four process criteria: (1) calcium utilization, (2) level of soluble calcium in the reactor effluent liquor, (3) sulfate precipitation, and (4) the dewatering properties of the waste solids produced. More than 35 batch and continuous flow runs were made over a range of reactor feed liquor compositions and reactor operating conditions. The purpose of these runs was to determine how major process variables affected the reactor performance in order to establish a set of operating conditions that would ensure:

- better than 90% calcium utilization with regeneration to hydroxide concentrations above 0.08M;
- less than 50 ppm of supersaturation of calcium with respect to gypsum in the reactor effluent liquor; and
- waste solids which could be filtered to a minimum of 50% solids and would provide a clear liquor overflow upon settling.

The limitation on soluble calcium levels is intended to minimize plugging of lines in the reactor and dewatering systems and reduce scale potential in the scrubber. A minimum of 50% solids in the filter cake would also ensure acceptable cake washing and handling properties.

a. Batch Experiments

The batch runs were made to verify that an equilibrium hydroxide level in excess of 0.10M could be achieved by reacting 0.5M Na_2SO_4 with hydrated lime and to confirm that supersaturation with respect to gypsum could be controlled. A concentration of 0.5M Na_2SO_4 was chosen because previous work by ADL[9] and General Motors[9] indicates that hydroxide levels of about 0.15M should be achievable. Hydroxide levels greater than 0.10M are desirable in order to reduce pumping rates and minimize tank sizes.

A total of 12 batch experiments was conducted using lime/Na_2SO_4 feed stoichiometries ranging from 0.05-0.25 mole $Ca(OH)_2$/mol Na_2SO_4. In a number of the runs at the higher stoichiometries, product solids were also added to study the effects of seeding. All runs were made at temperatures in the range of 45°C to 50°C.

Most experiments were limited to 30-minute reaction times, starting with reactant liquor pH levels of 3.8 (adjusted by sulfuric acid). A few runs were made starting at a pH of 7.4, and in one run the reaction time was extended to 60 minutes. Longer batch reaction times would translate into excessively long holdup times for continuous flow reactor systems, particularly those involving single CSTR's. Such long holdup times would adversely affect system design and capital costs.

Equilibrium Hydroxide

Figure VII-3 shows the effects of lime/Na_2SO_4 feed stoichiometry and the addition of product solids on the level of hydroxide produced in these batch tests. The product solids added in these runs were analyzed for available calcium hydroxide and the calcium hydroxide contained in the solids has been included in the calculation of the lime/Na_2SO_4 feed stoichiometry. In all experiments at lime/Na_2SO_4 feed stoichiometries below 0.17, lime utilization was on the order of 90% or greater. The presence of additional nucleation sites created by product solids noticeably increased the utilization of lime and the level of hydroxide achieved. Extending the reactor holdup time to 60 minutes did not appear to increase lime utilization significantly.

The maximum level of hydroxide attained in these batch experiments was 0.145M, which was reached when product solids were added to the reaction mix. It is apparent from the results of these experiments that 0.145M closely approaches the equilibrium hydroxide concentration for the experimental conditions. It is also consistent with the results from previous ADL work.

For the sulfate regeneration reaction:

$$Ca(OH)_2 + Na_2SO_4 + 2H_2O \rightleftarrows CaSO_4 \cdot 2H_2O + 2NaOH \qquad (12)$$

the equilibrium constant, K_{eq}, is given by:

$$K_{eq} = \frac{(a_{OH^-})^2}{(a_{SO_4^=})}$$

where the activity of the hydroxide and sulfate ions are:

$$a_{OH^-} = \gamma_{OH^-} [OH^-]$$

and

$$a_{SO_4^=} = \gamma_{SO_4^=} [SO_4^=]$$

Here the activity coefficients, γ_{OH^-} and $\gamma_{SO_4^=}$, are a function of the hydroxide and sulfate ions, respectively; the total ionic strength, and the temperature.

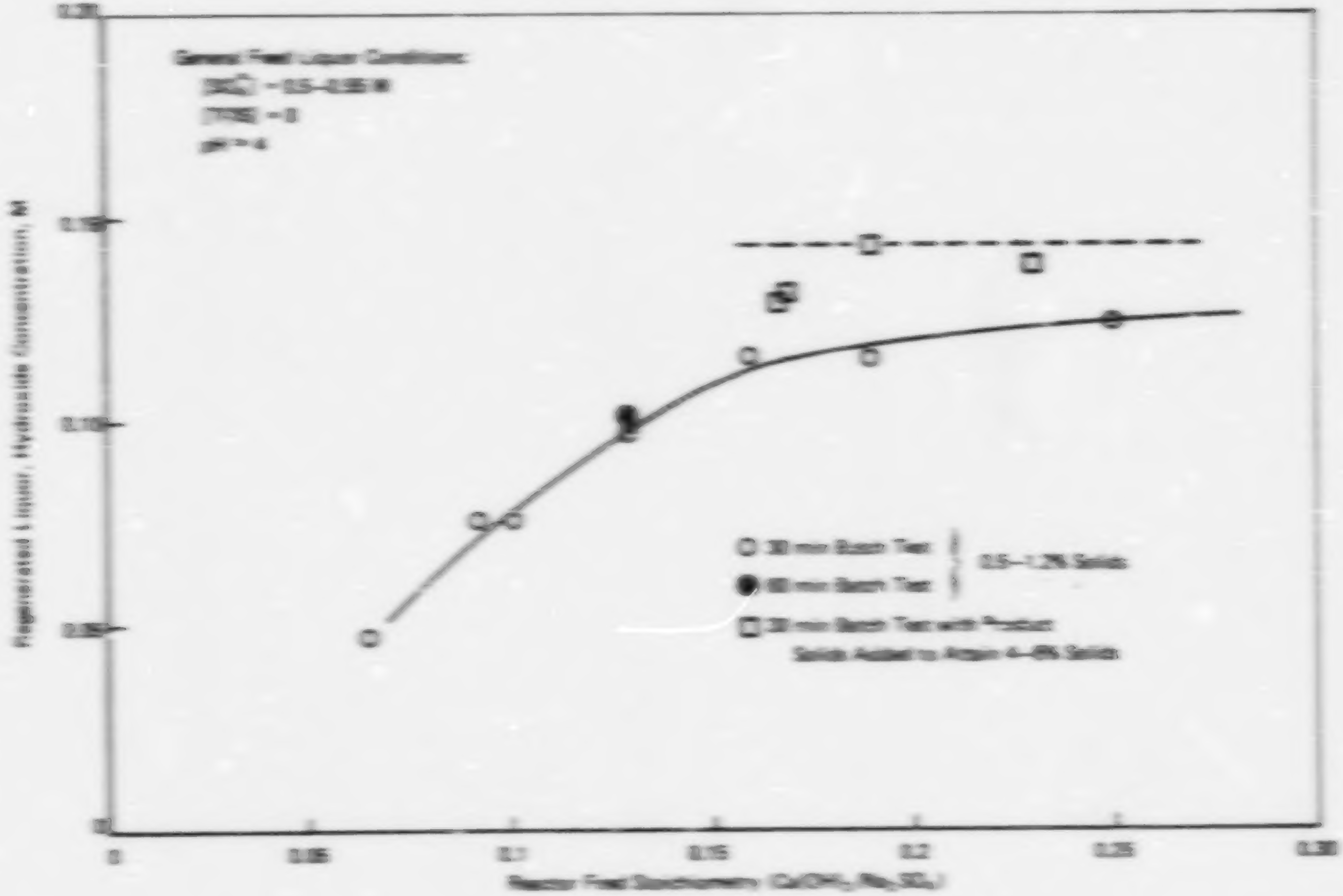

FIGURE VII-6 PRELIMINARY BATCH EXPERIMENTS
DILUTE MODE

The equilibrium ratio of hydroxide and sulfate concentrations, then, is given by:

$$\frac{[OH^-]^2}{[SO_4^=]} = K_{eq} \frac{\gamma_{SO_4^=}}{(\gamma_{OH^-})^2} \triangleq K_{eq}'$$

where K_{eq}' is a function of ionic strength and temperature.

Data previously obtained in batch experiments performed by ADL for the Illinois Institute for Environmental Quality[5] indicate the sensitivity of the reaction equilibrium to temperature and sulfate concentration. These data are summarized below along with the data from this study.

		Equilibrium Concentrations (M)			
Study	Temperature (°C)	$[SO_4^=]$	$[OH^-]$	$[Ca^{++}]$	$\frac{[OH^-]^2}{[SO_4^=]}$
IIEQ	30	0.47	0.155	0.017	0.051
EPA	45	0.45	0.145	0.018	0.047
IIEQ	71	0.47	0.110	0.020	0.026
IIEQ	71	0.25	0.090	0.0165	0.032

Calcium Supersaturation

In almost all runs the concentration of soluble calcium in the product slurries ranged from 680-750 Mg Ca^{++}/l. This corresponded in most cases to less than 50 ppm supersaturation with respect to gypsum. (Calcium saturation levels were determined by introducing an excess of gypsum crystals into the product slurries.) Only in the run where the reaction was started at a pH of 7.6 (with a reaction time of 30 minutes) was significant supersaturation observed. The supersaturation may be attributable to the slow generation of seed crystals. In an analogous run in which product solids were added to raise the suspended solids level from about 0.8% to about 3.5%, there was no supersaturation after 30 minutes of reaction.

b. Continuous Flow Reactor Runs

The matrix of experimental conditions covered in the open-loop, continuous flow reactor runs is given in Table VII-8. This matrix of experiments was designed to evaluate absorbent regeneration in the two different dilute mode options previously discussed -- the direct regeneration of scrubber bleed liquor, and the regeneration of liquor after oxidation of TOS. Two nominal reactor feed TOS levels were selected as representative of each of these two options -- 0.0-0.01M TOS for operation with oxidation and 0.04-0.05M TOS for operation without oxidation. Two additional runs were also made at 0.07M and 0.13M TOS. The range of compositions examined is summarized below.

TABLE VII-8

EXPERIMENTAL MATRIX FOR OPEN-LOOP, DILUTE MODE REACTOR TESTS

Nominal Feed Liquor Composition			Run	Reactor Configuration		Lime Feed Stoichiometry
[SO$_4^=$], M	[SO$_3^=$], M	pH	No.	Holdup/Type (min.)/-	Solids Recycle	(% of req't for 0.15M OH$^-$)
0.25	0.05	5.8	502	30/CSTR	—	21
0.25	0.25	5.8	501	30/CSTR	—	35
0.25	0.15	5.8	507	30/CSTR	—	67
0.25	0.05	5.8	505	5 + 30/ADL	—	52
0.25	0.05	5.8	504	60/CSTR	—	115
0.25	0.05	5.8	506	5 + 50/ADL	—	57
0.5	0	4	510	30/CSTR	—	73
0.5	0	4	513	30/CSTR	—	110
0.5	0	4	522	30/CSTR	—	77
0.5	0	4	521	60/CSTR	—	78
0.5	0	4	525	60/CSTR	—	95
0.5	0	4	524	60/CSTR	✓	98
0.5	0.05	5.8	511	30/CSTR	—	60
0.5	0.05	5.8	515	30/CSTR	—	75
0.5	0.05	5.8	516	5 + 60/ADL	—	42
0.5	0.05	5.8	517	5 + 60/ADL	—	40
0.5	0.05	5.8	518	5 + 60/ADL	—	58
0.5	0.05	5.8	519	60/CSTR	✓	66
0.5	0.05	5.8	520	120/CSTR	✓	75
0.5	0.15	5.8	512	30/CSTR	—	72
0.75	0	4	514	30/CSTR	—	115
0.75	0	4	523	60/CSTR	—	82
0.75	0.05	5.8	503	30/CSTR	—	83

A sulfate level of 0.5M was chosen as the basis for this continuous flow reactor study. A few exploratory runs were also made at nominal sulfate levels of 0.25M and 0.75M in order to determine the effect of sulfate concentration on reactor performance. The pH of the feed was adjusted depending upon the concentration of TOS. At 0.05M TOS in the reactor feed, the feed liquor pH was adjusted to 5.8, which represents a bisulfite-to-sulfite ratio of about 5:1. In all but one run involving little or no TOS, the pH was adjusted to approximately 4. This corresponds to an acidity of roughly 0.015M, a level that would be achieved with partial neutralization prior to, or during, oxidation of the scrubber bleed. Thus, the basis for the matrix of tests shown in Table VII-8 is summarized as follows:

	Nominal Composition of Reactor Feed Liquors	
Component	Without Oxidation	With Oxidation
TOS	0.05, 0.07, 0.13	0, 0.01
pH	5.8	4 and 6.5
$SO_4^=$	0.25, 0.5, 0.75	0.5, 0.75
Ca^{++}	0 and 500	500

In addition to the range of reactor feed compositions, a number of reactor parameters were also varied: reactor type (ADL two-stage reactor system, CSTR), solids recycle (to 4% solids), reactor holdup (30-120 minutes), and lime feed stoichiometry (20% to 115% of that required to regenerate 0.15M OH^-, the equilibrium level of hydroxide determined in the batch experiments for reaction with 0.5M sulfate). This equilibrium level of hydroxide is used as a normalizing factor to put the range of lime feed rates used in all runs on a common basis. However, it is realized that the equilibrium level of hydroxide will vary with ionic strength and changes in the apparent solubility products of gypsum and calcium hydroxide.

The results of this series of continuous flow tests and the implications of these results to reactor design and operation are discussed in the following sections in terms of the four performance criteria previously cited: calcium utilization, sulfate precipitation, calcium supersaturation, and waste solids properties.

Calcium Utilization

Figure VII-6 summarizes the utilization of calcium observed over the range of liquor compositions and reactor operating conditions. In this plot of lime utilization as a function of lime feed stoichiometry there are distinctly different functional relationships apparent for 0.25M $SO_4^=$ and 0.5-0.75M $SO_4^=$. The utilization of calcium is consistently higher at the

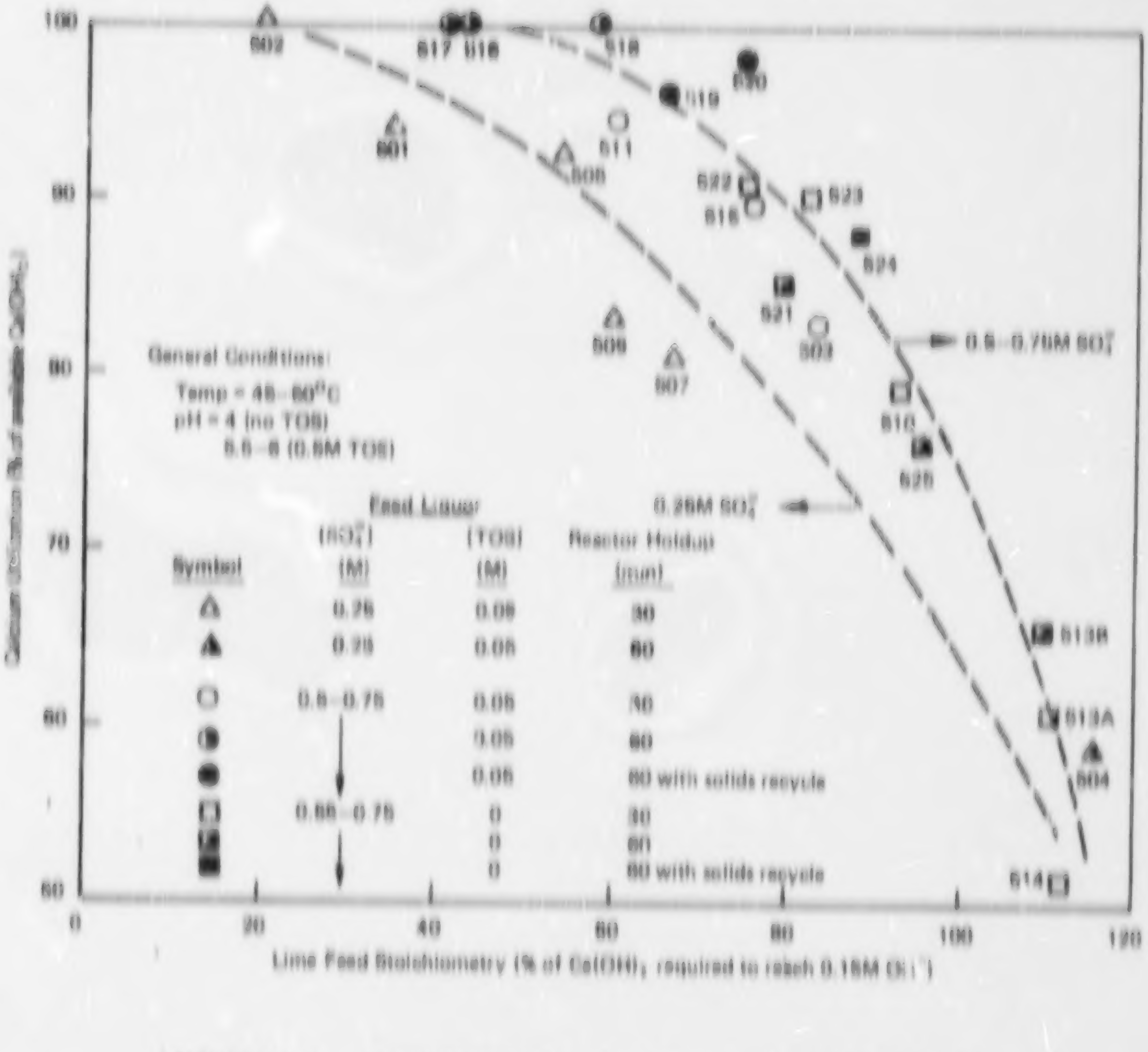

FIGURE VII-6 CALCIUM UTILIZATION IN CONTINUOUS, OPEN-LOOP RUNS

higher sulfate concentrations for equivalent lime stoichiometries. This can be attributed to reduced rates of reaction at the lower sulfate level, due to the lower equilibrium levels of hydroxide. The results show that at 0.25M sulfate, calcium utilization suffers when the lime feed rates are greater than that required to produce hydroxide levels above 0.05M. This is shown more clearly in Figure VII-7, in which lime utilization is plotted as a function of the hydroxide concentration achieved. Thus, if it is necessary or desirable to regenerate to 0.08M OH^- or higher, the sulfate concentration must be on the order of 0.5M.

At 0.5M sulfate, better than 90% lime utilization can be quite readily attained with regeneration to hydroxide levels slightly higher than 0.10M OH^-. However, in order to ensure 90% utilization with reactor holdup times on the order of 60 minutes or less, the lime feed stoichiometry must be maintained at or below 83% of that required to regenerate 0.15M hydroxide. That is, a reasonable practical limit for regeneration is about 0.12M OH^-. This is clearly indicated in Figure VII-7.

Lime feed stoichiometry and sulfate concentration were found to be the two most important factors affecting lime utilization. By comparison, the four other variables covered in these runs appear to have little discernible effect on lime utilization -- reactor type (ADL versus CSTR), liquor holdup time in the reactor (30 minutes versus 60 minutes), TOS concentration (0-0.13M), and recycle of product solids. The data in Figure VII-6 suggest that some gains in utilization can be made by increasing the reactor holdup time from 30 minutes to 60 minutes (or higher) and by recycling product solids. The data suggest that at 0.5M sulfate, operation with 60-minute holdup and with solids recycle might increase lime utilization by 5% over that achieved with a 30-minute holdup and with no solids recycle.

The fact that there is little effect of TOS concentration up to 0.13M TOS on lime utilization is somewhat surprising. The runs that were made with TOS in the reactor feed liquor also had high acidity levels in the feed liquor compared with those runs involving little or no TOS. For example, a typical reactor feed containing 0.05M TOS had a pH of about 5.8 and on the order of 0.045M titratable acidity, while a typical reactor feed with no TOS had a pH of about 4 but had only about 0.015M titratable acidity. In regenerating to a hydroxide level of 0.12M, the liquor with TOS would consume about 30% of the lime in neutralizing the acidity, while the liquor with no TOS would consume about 10% of the lime for neutralization. Since the neutralization reaction is virtually immediate, it would be expected that the runs with 0.05M TOS would exhibit higher lime utilizations. The results do not confirm this; if anything, there is a tendency for the runs with TOS to have slightly lower utilizations (Figure VII-7).

This agrees with laboratory results which indicate that low TOS levels retard the reaction rate. The higher lime utilization in runs without TOS may be related to the fact that in the presence of low levels of TOS, the solids are a mixture of calcium sulfite and sulfate which could supersaturate more easily. Such supersaturation, if not avoided, can retard

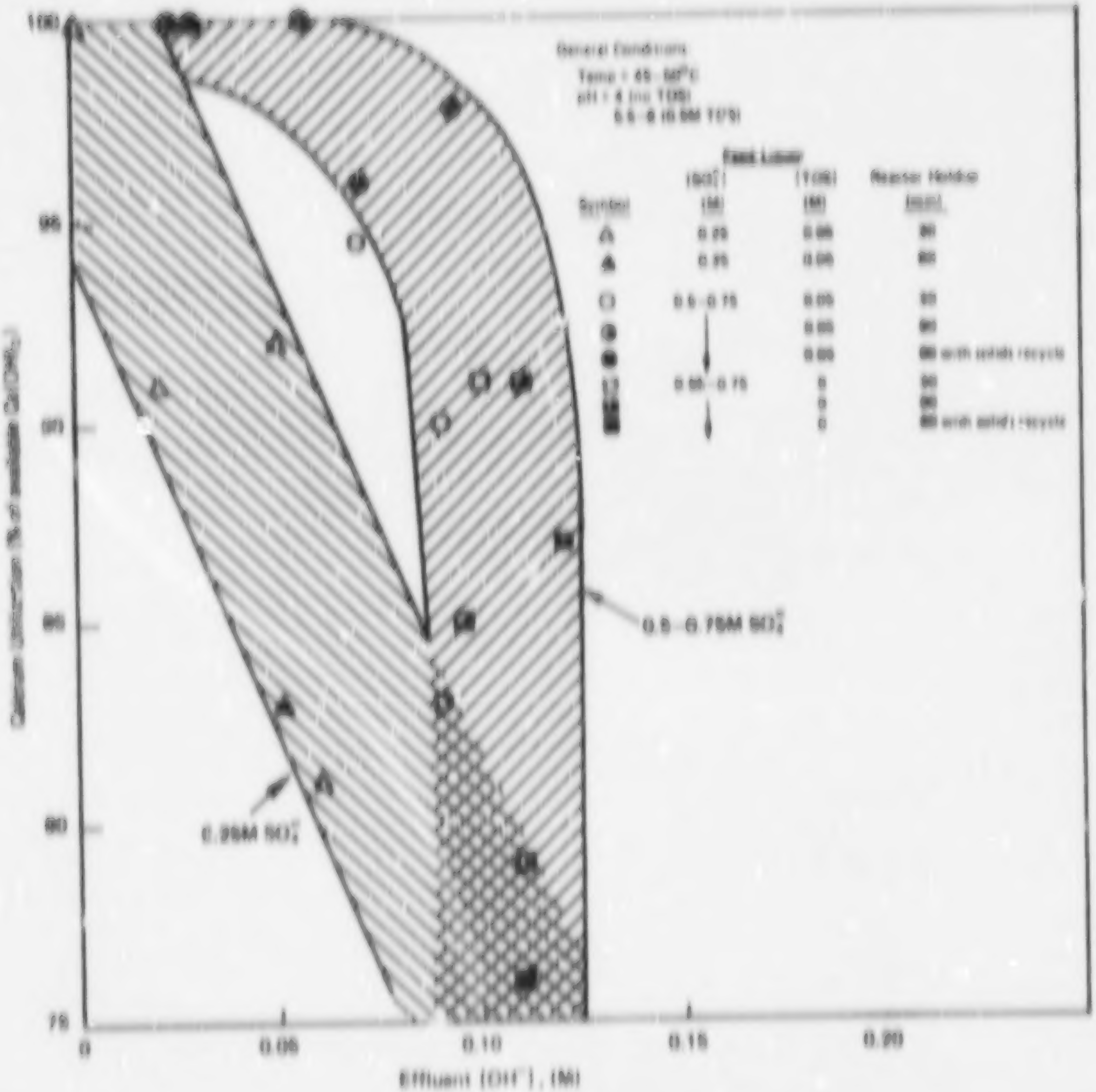

FIGURE VII-7 HYDROXIDE CONCENTRATION VS CALCIUM UTILIZATION IN CONTINUOUS, OPEN LOOP EXPERIMENTS

the rate of lime dissolution and thereby the overall rate of reaction, resulting in lower lime utilization. The question of supersaturation is discussed later.

Sulfate Precipitation

The potential for sulfate precipitation during absorbent regeneration is substantially greater in dilute mode operations than in concentrated mode operations. In fact, since sodium hydroxide can be regenerated from pure sodium sulfate by reaction with lime, the opportunity exists for producing a relatively pure calcium sulfate waste product by oxidizing the TOS prior to regeneration.

The effects of sulfate and TOS concentration in the reactor feed liquor on the level of sulfate in the waste solids are shown in Figures VII-8 and VII-9. Figure VII-8 shows a strong dependence of sulfate precipitation on soluble sulfate concentration at soluble sulfate levels greater than 0.3M. Figure VII-9 shows that, for reactor feed liquors containing 0.5M $SO_4^=$, there is a strong sensitivity of sulfate precipitation to soluble TOS concentration at TOS levels below about 0.04M. Each of these relationships in Figures VII-8 and VII-9 represents but one of a family of parametric curves.

Similar relationships developed for the concentrated active sodium regime in previous laboratory and pilot plant test programs had indicated that sulfate precipitation equivalent to as much as 25% of the total calcium-sulfur waste salts could be reasonably achieved. This would be equivalent to keeping up with overall system oxidation rates on the order of 25-30% of the SO_2 removal (taking into account Na_2SO_4 losses in the waste cake).

Concentrated mode data on crystalline morphology and water of hydration indicate that the calcium sulfate at levels of up to about 25% of the calcium-sulfur salts is present as a solid solution or mixed crystal with calcium sulfite, and not as gypsum. The results shown in Figures VII-8 and VII-9 corroborate these concentrated mode results. The sulfate precipitation behavior suggests that there may be a change in the sulfate precipitation mechanism when conditions drive sulfate levels in the solids to greater than about 30%. It is likely that at below 30% the calcium sulfate is present as a solid solution or mixed crystal with calcium sulfite, and that above 30% the sulfate is precipitated as gypsum.

The exact liquor concentrations in the reactor ($[SO_4^=]/[SO_3^=]$ and total ionic strength) will dictate the point at which gypsum will begin to precipitate. While the fluctuations in the soluble TOS data on the reactor effluent preclude an accurate estimate of where this change may occur, the feed liquor data (Figures VII-8 and VII-9) suggest that this break point occurs at a feed ratio of sulfate-to-TOS of roughly 15-20 in the range of ionic strengths investigated.

The advantage of the dilute mode, therefore, lies in its potential for keeping up with oxidation rates in excess of 30% of the SO_2 removal.

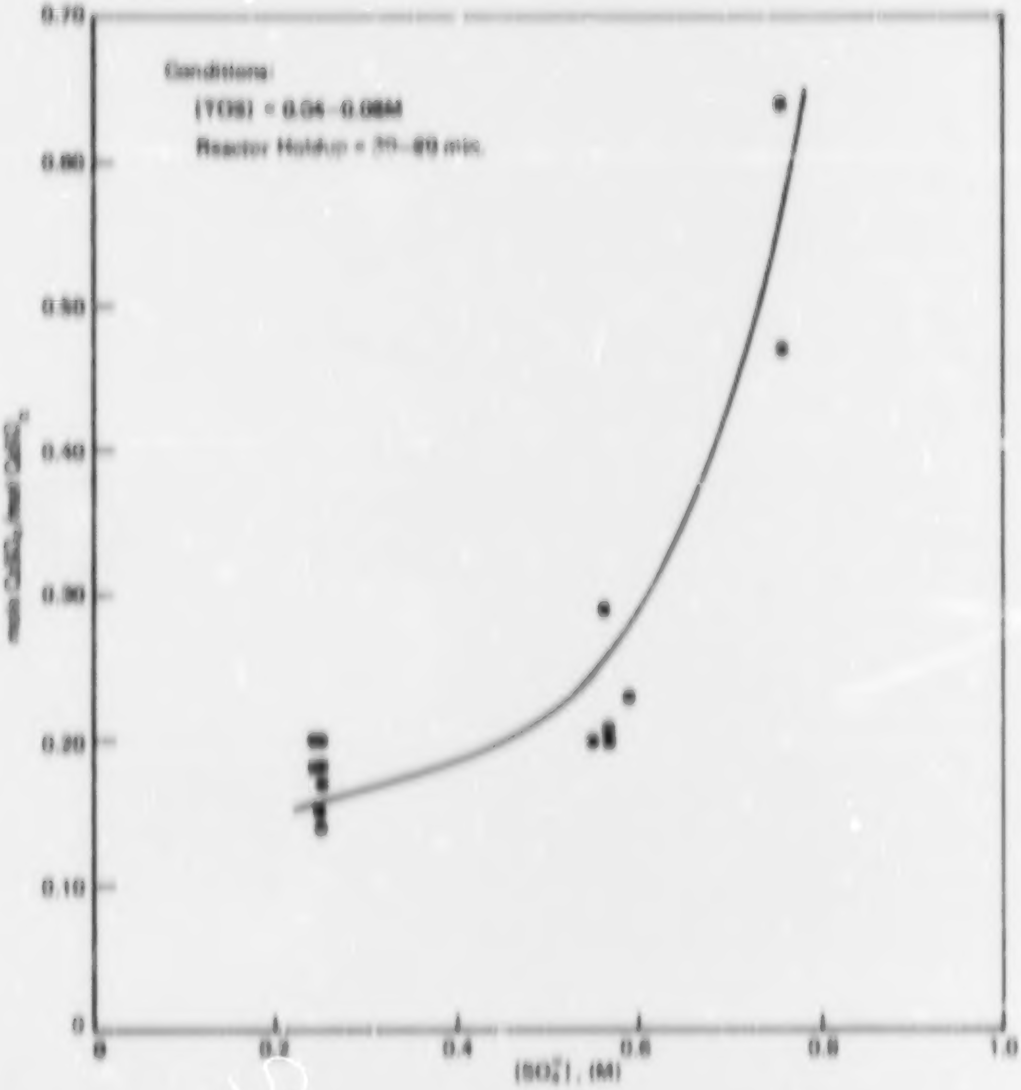

FIGURE VII-8 CALCIUM SULFATE PRECIPITATION AS A FUNCTION OF SOLUBLE SULFATE CONCENTRATION

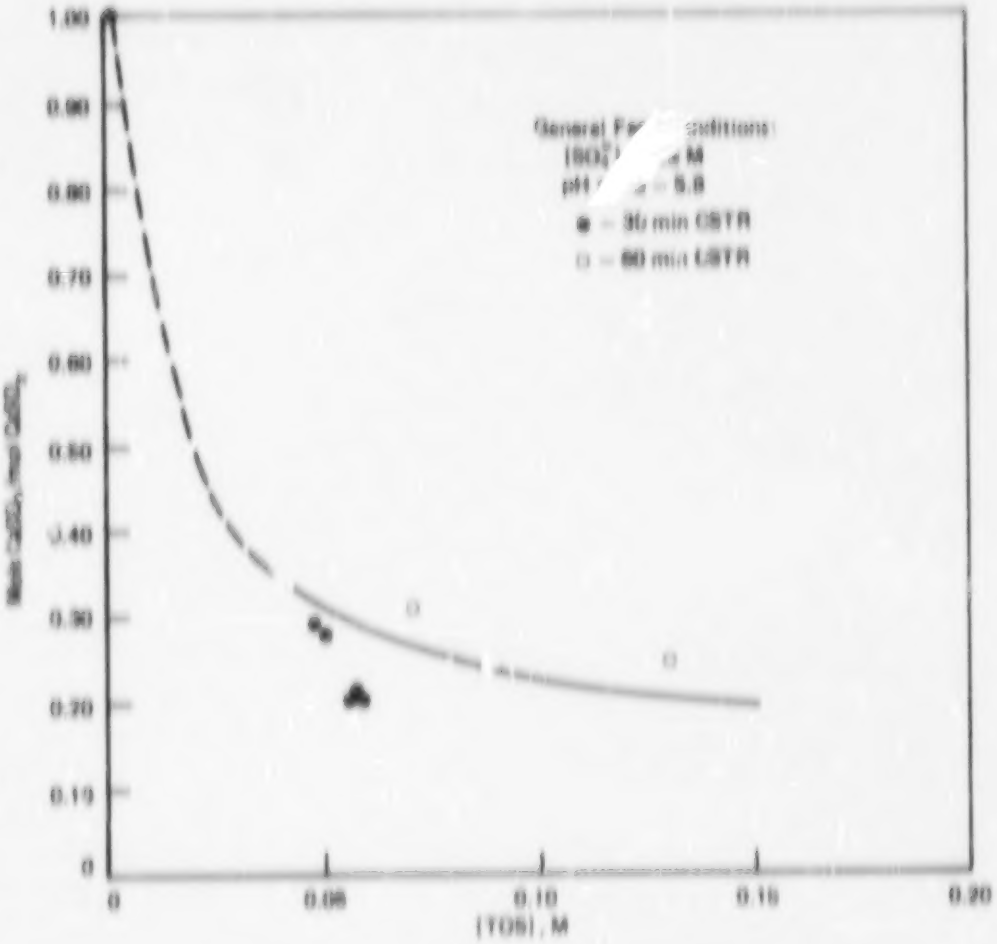

FIGURE VII-8 CALCIUM SULFATE PRECIPITATION VS TOS CONCENTRATION

Similarly, at 0.5M $SO_4^=$, oxidation rates of 30% would result in scrubber effluent TOS concentrations less than 0.05M. In a dilute mode application the system would probably be charged to a total sodium concentration consistent with the operational level of sulfate desired. If the scrubber bleed liquor were not intentionally oxidized, then the proportions of active sodium (TOS) and sulfate would vary according to the level of oxidation experienced. For example, with system oxidation rates of 50%, it would be necessary to operate the system at about 0.75M $SO_4^=$ if TOS levels of 0.05M were desired (Figure VII-8). On the other hand, if a 0.5M $SO_4^=$ level were desired, then TOS concentration in the scrubber bleed would be about 0.02M (Figure VII-9).

The data plots given in Figures VII-8 and VII-9 exhibit considerable data scatter. Some of this can be attributed to slight variations in sulfate and TOS concentrations. However, the data also cover a range of lime feed stoichiometries from 20% to 115% of that theoretically required to achieve 0.15M OH^-. The effect of lime stoichiometry on sulfate precipitation is shown in Figure VII-10 for sulfate levels of 0.25M and 0.57M. Although there is also scatter in these data which may amount to ± 15%, the data suggest some dependence of sulfate precipitation on lime stoichiometry at 0.57M $SO_4^=$. Sulfate levels in the solids generated with a lime feed stoichiometry of 40% are 10-30% higher than the sulfate levels above 60% stoichiometry. Here, 40% stoichiometry is roughly equivalent to regeneration to a hydroxide level of 0.02M. The effect of stoichiometry is similar to the one observed in the laboratory work in the concentrated lime mode. However, the number of data points is small, and the fact that a similar relationship is not seen at 0.25M sulfate indicates that more data would be required to confirm and explain these results.

Calcium Supersaturation

The levels of soluble calcium present in the reactor effluent liquor depended upon four factors: the concentration of TOS in the reactor feed liquor, the extent of regeneration, the solids holdup time in the regeneration reactor (both nominal fluid holdup and solids recycle), and the type of reactor system employed. The extent of regeneration (or lime feed stoichiometry) was of importance only in those runs in which there were appreciable levels of TOS in the reactor feed liquor. In these runs the reactor effluent liquor was unsaturated or just saturated with respect to gypsum when lime feed stoichiometries were low. At low stoichiometries the only sulfate being precipitated was in a solid solution or mixed crystal with calcium sulfite and the soluble calcium level in the liquor was controlled by the TOS concentration. However, when lime was fed at a rate sufficient to regenerate to above 0.06M hydroxide (a level which could not be reached by reaction with TOS alone), the effluent liquors tended to supersaturate with respect to gypsum.

In most cases, it is desirable to operate dilute mode systems at the highest hydroxide concentrations that can be realistically achieved in order to minimize liquor flows. A high priority in the pilot plant

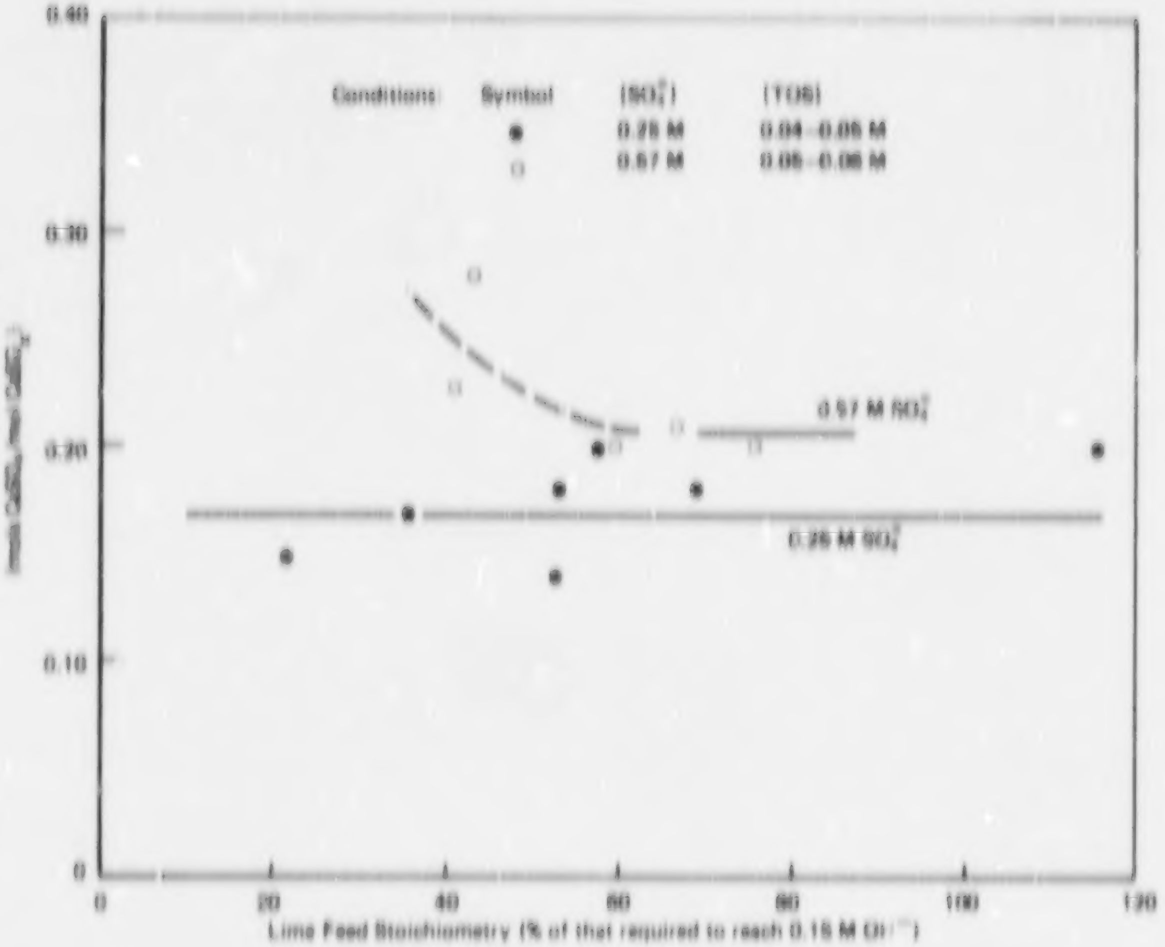

FIGURE VII–16 CALCIUM SULFATE PRECIPITATION VS LIME FEED STOICHIOMETRY

work was therefore placed on establishing reactor conditions that would allow regeneration to greater than 0.06M OH^- without resulting in excessive supersaturation. Such supersaturation can cause scale deposition not only in the scrubber system, but also in the reactor system, dewatering equipment, and interconnecting piping. At hydroxide levels much below 0.06M OH^-, pumping costs and tank sizes become excessive.

Table VII-9 lists the operating conditions and soluble calcium levels for runs at nominal sulfate concentrations of 0.5M and 0.75M in which hydroxide levels greater than 0.06M were achieved. As previously discussed, such levels of hydroxide could not be satisfactorily achieved operating with 0.25M sulfate. The soluble calcium data shown in Table VII-9 represent averages of two or three concentrations measured during each run. In most cases the individual measurements differed by less than 0.0015M Ca^{++} (about 60 ppm).

The level of calcium supersaturation was determined from measurements of the soluble calcium concentrations in samples of the reactor slurry before and after mixing the slurry with an excess of gypsum crystals. The calcium saturation levels determined by this procedure are plotted as a function of sulfate concentration in Figure VII-11. Not surprisingly, the calcium saturation level increases with increasing sulfate concentration over the range of 0.25M to 0.75M sulfate. This increase is due to the marked effect of ionic strength on the apparent gypsum solubility product.

The data scatter in Figure VII-11 arises from slight differences in temperature at which the saturation measurements were made and from variations in ionic strength due to different TOS and hydroxide concentrations. The error in the calcium determinations themselves is estimated to be on the order of ± 20 ppm.

The soluble calcium levels in the runs shown in Table VII-9 ranged from 720 ppm to about 950 ppm, a range which corresponds to about 100 ppm to 350 ppm supersaturation. The highest soluble calcium levels occurred in runs using a CSTR with a 30 minute holdup time. The lowest calcium levels occurred in runs using either a CSTR with a 60 (or 120) minute holdup time and recycle of product solids (to 4%), or in the ADL reactor system with a 60 minute holdup time. However, supersaturation occurred in all of the open-loop runs in which regeneration was carried out to above 0.06M hydroxide.

The diagrammatic representation of the calcium data in Figure VII-12 summarizes the relative effects of feed liquor composition, holdup time, and solids recycle on calcium supersaturation in a CSTR. The decrease in supersaturation with increasing fluid holdup time and product solids recycle is clear. There appears to be little effect, if any, though, of sulfate concentration on supersaturation over the range 0.5-0.75M $SO_4^=$. However, the data suggest that low concentrations of TOS increase supersaturation slightly over the equivalent case where there is no TOS. This may actually be due to the crystalline form of product solids rather than simply the presence of TOS. Runs in which a significant fraction of the

TABLE VII-9

CALCIUM SUPERSATURATION IN OPEN-LOOP REACTOR RUNS

Nominal Feed Liquor Composition			Reactor Operation		Effluent Concentrations		Avg. Ca^{++}	
$[SO_4^=]$ (M)	[TOS] (M)	Run No.	Holdup/Type (min.)/-	Solids Recycle	$[OH^-]$ (M)	Avg. $[Ca^{++}]$ (mg/l)	Supersat. (mg/l)	Predominant Solids Form[a]
0.5	0.05	511	30/CSTR	—	0.07	960	320	S & P
0.5	0.05	515	30/CSTR	—	0.09	850	240	S & P
0.5	0.05	518	5 + 55/AGL	—	0.06	720	120	S & P
0.5	0.05	519	60/CSTR	to 4%	0.07	800	200	S & P
0.5	0.05	520	120/CSTR	to 4%	0.095	780	180	S & P
0.5	0.01	525	60/CSTR	—	0.125	920	260	P
0.5	0	510	30/CSTR	—	0.11	780	200	G
0.5	0	513	30/CSTR	—	0.095	950	360	P & G
0.5	0	521	60/CSTR	—	0.095	760	120	G
0.5	0	524	60/CSTR	to 4%	0.12	720	80	G
0.75	0	514	30/CSTR	—	0.08	800	220	G
0.75	0	522	30/CSTR	—	0.10	880	230	G
0.75	0	523	60/CSTR	—	0.11	860	180	P & G

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[a] S = $CaSO_3 \cdot 1/2H_2O$; P = mixed sulfite/sulfate or $CaSO_4 \cdot 1/2H_2O$; G = $CaSO_4 \cdot 2H_2O$

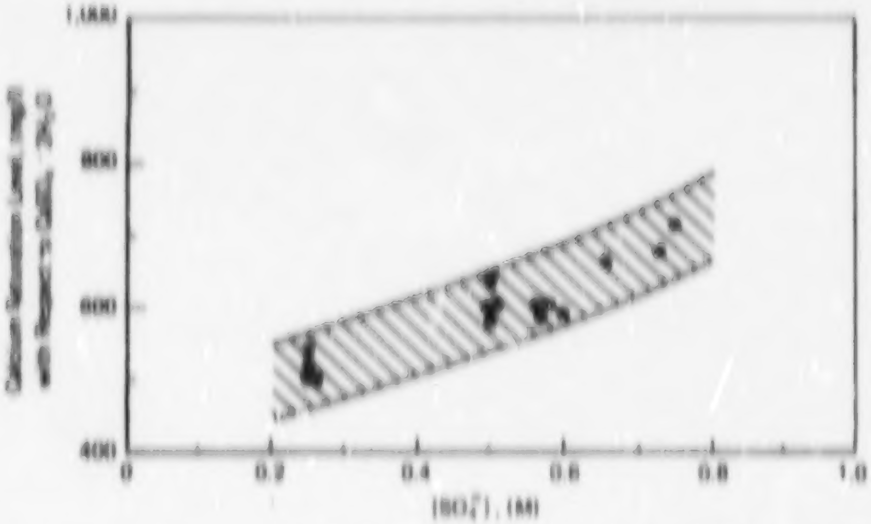


FIGURE VII-11 CONCENTRATION OF SOLUBLE CALCIUM AT SATURATION VS. SOLUBLE SULFATE CONCENTRATION

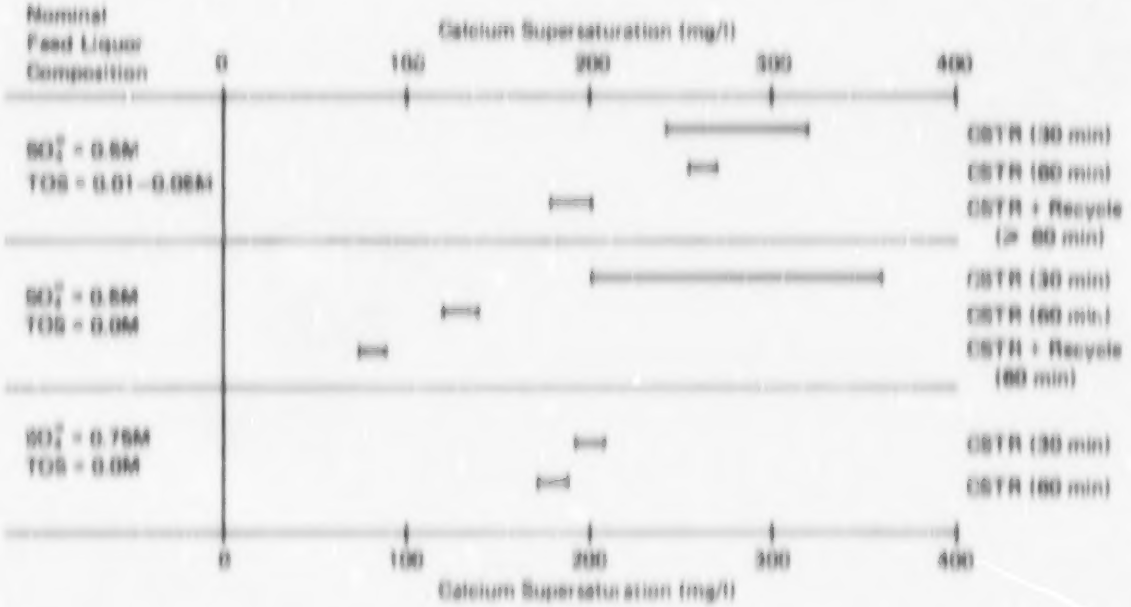


FIGURE VII-12 CALCIUM SUPERSATURATION IN RUNS USING A CSTR

solids were in the form of hemihydrates (either pure calcium sulfate or mixed calcium sulfite/sulfate) showed greater degrees of supersaturation than corresponding runs in which gypsum (calcium sulfate dihydrate) was formed. In the presence of appreciable concentrations of TOS (> 0.05M), the hemihydrate form is clearly due to the dominance of the mixed sulfite/sulfate product and its seeding effects. The reason for the formation of calcium sulfate hemihydrate when there were very low levels of TOS or no TOS (runs 513, 523, and 525) is not clear. It may have been due to variations in temperature. Both the hemihydrate and dihydrate forms are known to exist in the temperature range of these runs (45-55°C). The hemihydrate form is generally considered to be metastable at these temperatures and its existence could simply have been a transitory phenomenon.

Although saturation was not achieved in any of the runs, the results indicate what steps can be taken to minimize supersaturation. These are:

- fluid holdup times of 60 minutes or more;
- elimination of TOS prior to regeneration (by oxidation of the scrubber bleed);
- recycle of product solids to achieve levels of 4% or greater suspended solids; and/or
- use of a multistage reactor system.

All of these were, in fact, tried in the closed-loop runs. As will be discussed later, supersaturation was eliminated by the recycle of product solids to suspended solids levels greater than 5% in conjunction with a holdup time of 90 minutes. The ADL reactor system without solids recycle did not eliminate supersaturation but did maintain calcium levels within 100 ppm of saturation (typically about 50 ppm higher than saturation).

Solids Properties

Two parameters were used as a measure of the dewatering properties of the solids: the initial settling rate of the solids, and the density of the settled solids layer after one hour of settling. These two parameters are plotted in Figures VII-13 and VII-14 for the open-loop runs. It should be noted that these data are of importance only in terms of the relative values over the range of conditions. The absolute values of the parameters should not be compared with similar data obtained in the concentrated lime mode. The slurry concentrations are different, and slurry concentration can strongly affect settling rates (hindered settling versus free settling, etc.).

In general, both the settling rates and densities of settled solids decrease with increasing TOS concentration. This is consistent with the widely held belief that calcium sulfite does not settle or dewater as well as calcium sulfate and that the presence of calcium sulfite in

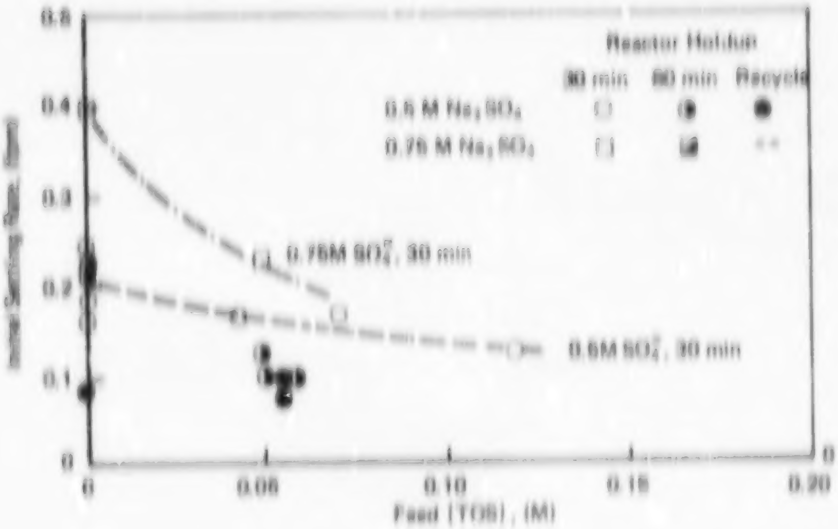


FIGURE VII-13 SOLIDS SETTLING RATE VS. FEED TOS LEVEL

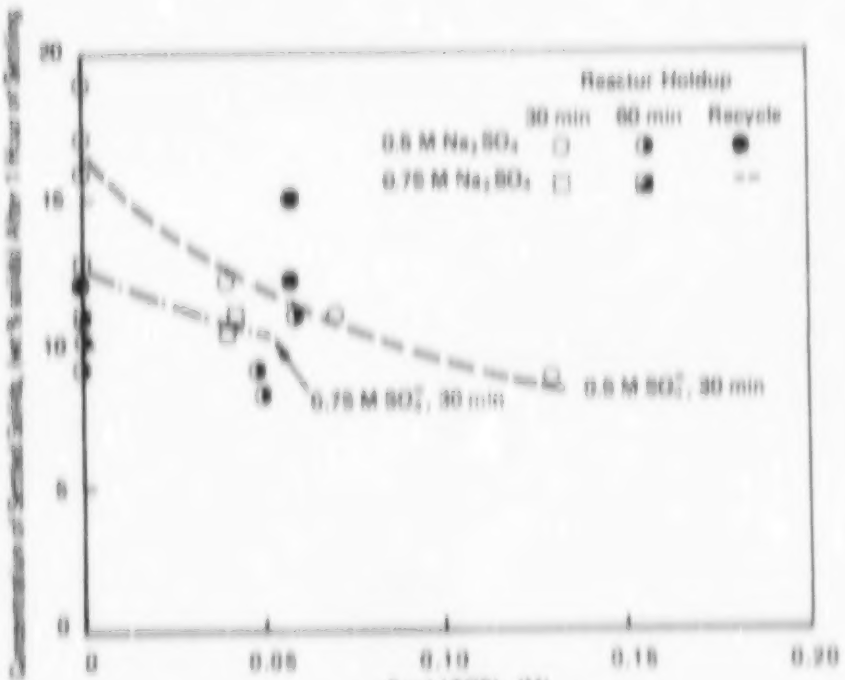


FIGURE VII-14 CONCENTRATION OF SETTLED SOLIDS VS. FEED TOS LEVEL

calcium sulfate cakes reduces the filterability of waste solids. However, it should be noted that exactly the opposite effect is true in the concentrated lime mode -- the dewatering properties of the solids deteriorate with increasing sulfate concentration.

The effect of sulfate concentration on solids properties in the dilute mode cannot be determined based upon the results in Figures VII-13 and VII-14. The initial settling rate of the solids appears to increase by increasing sulfate concentration from 0.5M to 0.75M, but the density of the settled solids tends to decrease. Such behavior might suggest that slightly larger crystals are formed at 0.75M, but that those do not pack as well under a one gravity force.

The effect of fluid holdup time on solids properties is similar to that observed in the concentrated lime mode. Solids properties tend to deteriorate when the reactor holdup time is increased from 30 minutes to 60 minutes. Recycling product solids, on the other hand, tends to enhance solids properties, apparently by allowing crystals to grow. The fact that the initial settling rates were slower in runs with solids recycle is due primarily to the fact that the suspended solids level was eight times higher in these runs. The presence of this quantity of solids hindered the normal free fall observed in the thinner reactor slurries. In runs with solids recycle the settling rates of solids per unit area (tons/ft^2-hr) were equivalent to or greater than those in runs without solids recycle, but the increase in the settling rates was not sufficient to compensate for the greater quantity of solid that the thickener would have to handle in a solids recycle mode. Therefore, use of solids recycle would increase the required thickener area by a factor of two to five.

3. Evaluation of Overall System Performance (Closed-Loop Operation)

The results of the open-loop testing of the reactor system demonstrated that in a dilute mode operation the sulfate concentration should be maintained at about 0.5M or higher so that hydroxide levels of 0.1M can be relatively easily achieved, and that elimination of all soluble TOS prior to regeneration (by oxidation of sulfite to sulfate) improves solids properties and reduces the potential for supersaturation. These two conditions, then, provided the basis for the closed-loop dilute mode runs.

a. Description of System Operation

Three closed-loop runs were made at inlet SO_2 levels ranging from 700 ppm to 1,100 ppm. Dilute mode operations are most applicable to low-sulfur coal operations where high rates of sulfite oxidation occur that cannot be readily handled by concentrated modes.

The first two runs, 601 and 602, were relatively short -- each lasting only a few days. These runs were exploratory in nature, being geared toward verifying the results of the open-loop tests and establishing appropriate operating conditions for the third 500-hour closed-loop run

(run 620). In each run the system was charged with liquors with compositions based upon the expected steady-state conditions of each run.

Except for the type of reactor system used, the process configuration in all of the closed-loop runs was essentially the same. Figure VII-15 shows a schematic of the basic equipment arrangement.

The scrubber system consisted of a venturi followed by a tray tower containing either two or three trays. Two trays were used in runs 601 and 602, and three trays were used in run 620. The general operating parameters and flue gas conditions are listed in Table VII-10.

Regenerated liquor was fed to the tray recycle tank which served as a hold tank for liquor recirculated across the trays. A bleed from the recirculating liquor was sent forward to the venturi recycle tank. The rate of this bleed was set manually based upon pH of the venturi liquor (or SO_2 removal) and this rate set the overall feed forward through the integrated system. For the most part, the pH of the venturi recycle in all runs was typically in the range of 5.3 to 6.0.

A bleed stream of spent liquor from the venturi recycle line was sent to the air-sparged oxidation tank where most or all of the TOS was converted to sulfate. The rate of withdrawal of the bleed stream was controlled on the level of liquor in the venturi recycle tank.

The design and operation of the oxidation tank were based upon the results of a number of open-loop tests. Air was introduced at the bottom of the tank through a ring-shaped sparger at a rate equivalent to an oxygen:TOS stoichiometry ranging from 5:1 to 25:1 depending upon the concentration of TOS in the scrubber bleed. The pH of the oxidation tank was controlled between 4.5 and 10 using clarified regenerated liquor in order to prevent SO_2 off-gassing. The open-loop tests had shown that without at least partial neutralization of the oxidation tank liquor, the pH of the liquor would fall to below 4 causing appreciable SO_2 off-gassing equivalent to as much as 15% of the TOS fed to the oxidation tank. Partial neutralization in the oxidation tank, as shown in the open-loop testing of the regeneration reactor system, has very little, if any, effect on the reactor system performance and avoided the need for a sealed aeration tank vented to the scrubber inlet.

Two different aeration systems were used. In runs 601 and 602 the aeration tank had about a 30 minute holdup and pure oxygen was introduced into the liquor feed line to the system to assist in oxidation. In run 620 a tank with a two hour holdup time was used with no oxygen fed into the liquor line.

The oxidized scrubber bleed was fed by gravity to the regeneration reactor system where the liquor reacted with hydrated lime. The lime was metered to the reactor in the form of a dry solid. The lime feed rate was adjusted according to the pH of the reactor effluent in order to maintain the hydroxide concentration in the regenerated liquor in the 0.08M to 0.12M OH^- range.

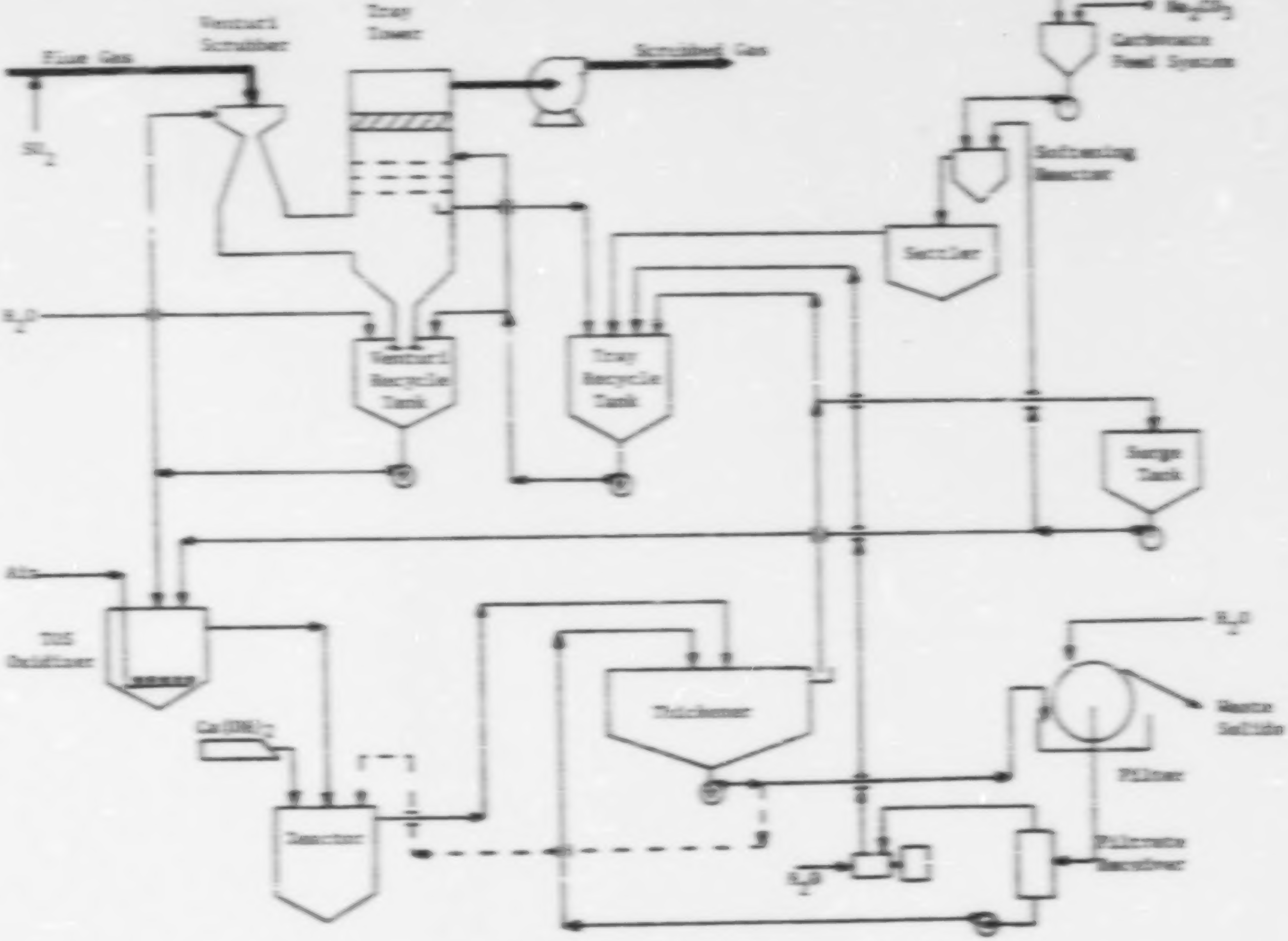

Flue Gas
SO_2
Venturi Scrubber
Tray Tower
Scrubbed Gas
MgO
Na_2CO_3
Carbonate Feed System
Softening Reactor
Settler
H_2O
Venturi Recycle Tank
Tray Recycle Tank
Surge Tank
Air
TDS Oxidizer
$Ca(OH)_2$
Reactor
Thickener
H_2O
Waste Solids
Filter
Filtrate Receiver
H_2O

FIGURE VII-15 PROCESS FLOW DIAGRAM FOR DILUTE LIME MODE PILOT PLANT OPERATIONS WITH TDS OXIDATION

TABLE VII-10

GENERAL OPERATING CONDITIONS FOR SCRUBBER SYSTEM

Inlet Flue Gas:	
SO_2 Level, (ppm)	700-1050
O_2 Level, (ppm)	5-9.5
Dry-Bulb Temperature, (°F)	340-470
Dew Point, (°F)	120-130
Venturi Operating Parameters:	
ΔP, (inches H_2O)	11-17
L/G, (gals./Macf sat'd)	10-20
Tray Tower Operating Parameters:	
ΔP, (inches H_2O/tray)	1.4-1.8
L/G, (gals./Macf sat'd)	5-10

The configuration of the reactor system was the primary difference among the closed-loop runs. In both runs 601 and 602 a simple CSTR with a two-hour holdup time was used. The long reactor holdup time was to ensure good utilization of lime and, hopefully, at the same time, allow sufficient time for desupersaturation of calcium. Solids recycle was also tested for a few hours at the end of run 602 using filter cake as the source of the recycle solids.

Run 620, which lasted about four weeks, was broken into two parts, each corresponding to the use of an entirely different reactor configuration. In the first part, run 620A, a CSTR with a 90 minute holdup time was used along with the recycle of solids from the thickener underflow. The rate of recycle was varied to study the effects of suspended solids levels on calcium desupersaturation. In run 620B the ADL reactor system with a 90 minute to total holdup time was used without solids recycle (first stage holdup = 10 minutes; second stage holdup = 80 minutes).

The waste solids generated in the reactor were dewatered using a standard thickener and rotary drum vacuum filter combination. The filter cake was washed to recover most of the sodium value occluded with the cake. The combined filtrate and wash water was returned to the thickener. A portion of the clarified overflow from the thickener was drawn off for use in neutralization of the oxidation tank. The remainder was returned to the scrubber system either directly or through the softening reactor.

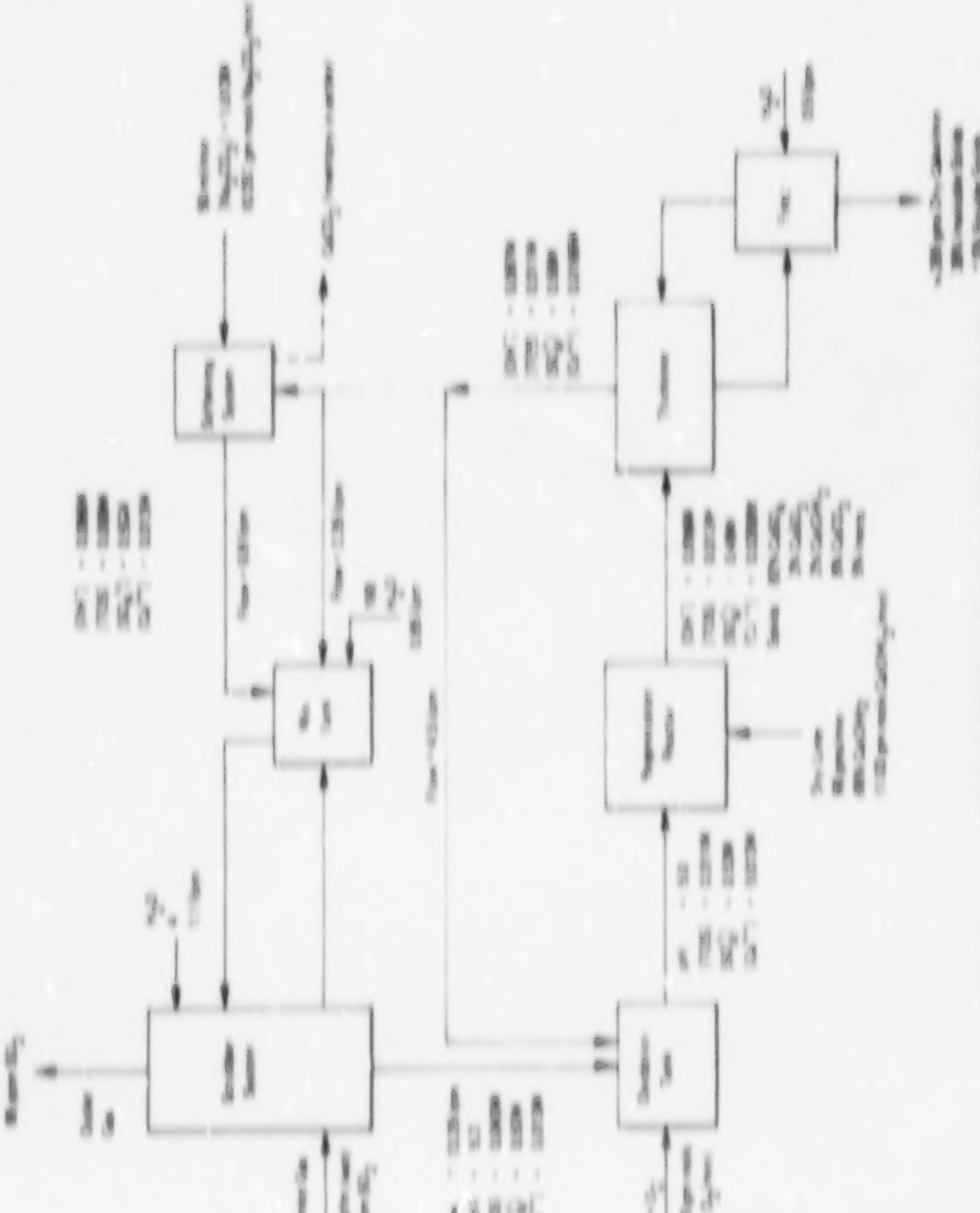
The soda ash makeup to the system was added to the softening reactor where it reacted with the soluble calcium in the clarified liquor producing calcium carbonate. The softening reactor was a simple CSTR with a holdup time of roughly 30 minutes. After settling out the calcium carbonate the softened liquor was passed to the tray recycle tank.

The overall effect of the soda ash softening step was to reduce the soluble calcium concentration in the combined liquor returned to the scrubber system by about 50 ppm. The amount of softening that could actually be accomplished in any run was dependent upon the rate of sodium loss in the filter cake, since this determines the rate of soda ash makeup.

b. Summary of System Performance

Table VII-11 summarizes the general operating conditions and overall system performance in the closed-loop operations, and Figures VII-16 and VII-17 show the compositions and flows of the process streams in runs 602 and 620A.

In general, the system performed reasonably well as long as the level of TOS in the system liquor was at or below 0.02M prior to absorbent regeneration. There were, however, a number of problems with scaling and scale potential. These are discussed along with the various aspects of system performance in the following sections.



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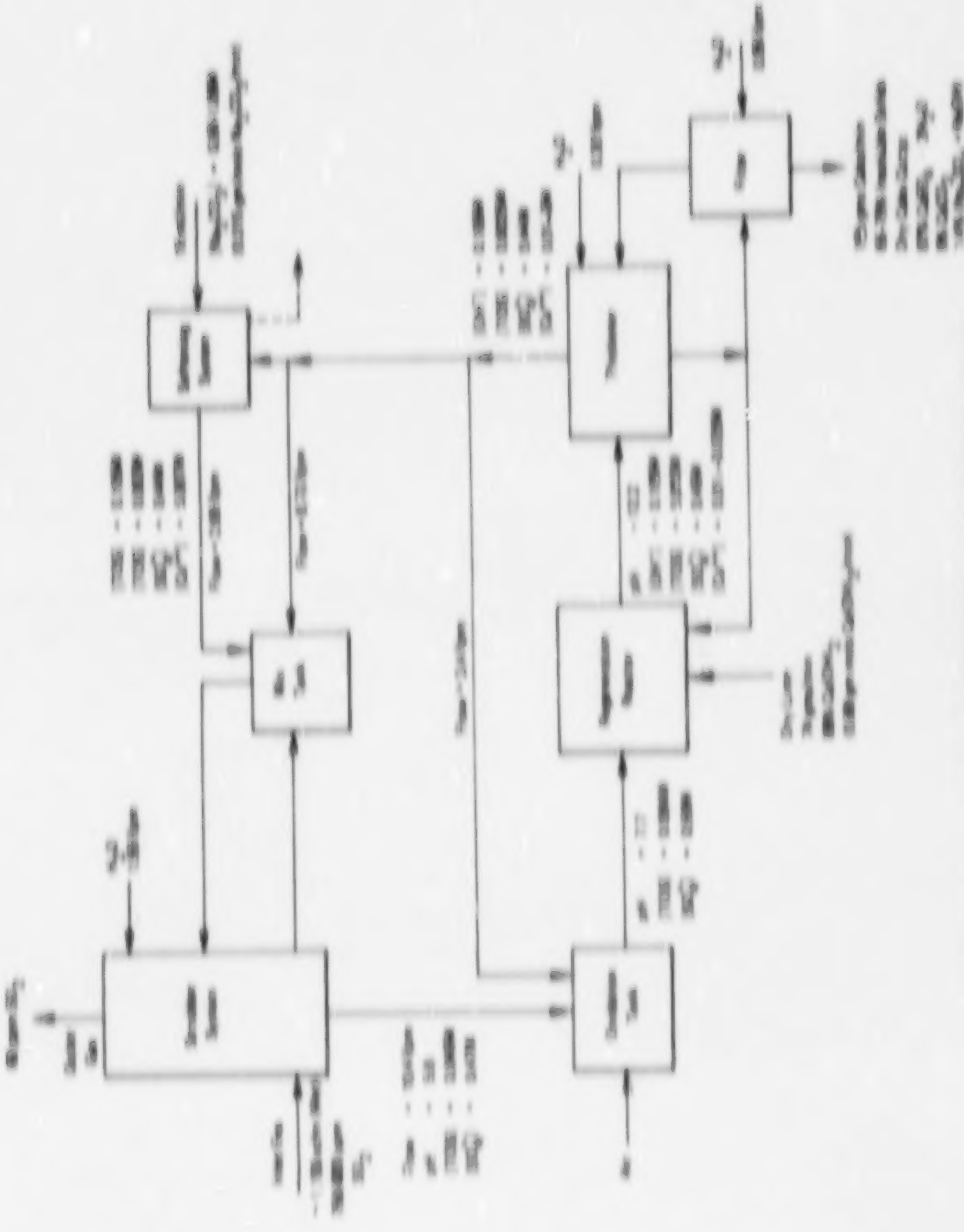

Scrubber System Performance

Over the range of inlet SO_2 levels covered in these runs (700-1,050 ppm) there was no difficulty in achieving SO_2 removal efficiencies of 90% or better. As would be expected, in run 620 (A and B) where three trays were used, SO_2 removal efficiencies were slightly higher (and outlet SO_2 levels correspondingly lower) than in runs 601 and 602 in which two trays were used. The fact that only about 90% removal was achieved with two trays and a venturi reflects the particular conditions under which the pilot plant was operated. The saturated flue gas exiting the scrubber was at a temperature of about 140-145°F, which is about 20-25°F higher than would normally be experienced in a normal boiler application. The higher operating temperature increases the vapor pressure of SO_2, making removal more difficult. The lower flue gas temperature in a full-scale system, plus the better stage efficiencies in a larger tray absorber (due to better gas/liquid distribution), would result in somewhat better SO_2 removal efficiencies than that observed in the pilot plant.

Except in run 601, oxygen levels in the flue gas were also set higher than would normally be experienced in an efficient boiler operation. The intent in these runs was to induce oxidation; the higher the level of oxidation in the scrubber system, the lower the load on the oxidation system. As shown in Table VII-11, the oxidation in the scrubber system varied directly with the oxygen content of the flue gas -- from an equivalent oxidation of 200 ppm of SO_2 at 5-6% O_2 in run 601, to about 400 ppm of SO_2 at 9-9.5% O_2 in run 602. The low oxidation rates experienced in the scrubber system in run 601 actually caused operational problems in the reactor system performance.

The major problems associated with the operation of the scrubber system were the control of pH and prevention of or minimization of potential for scale formation. These problems are closely related to the amount of oxidation occurring. In runs 620A and 602, for example, there was an appreciable amount of oxidation in the scrubber system (55-65% of the SO_2 removed). As a result, there was very little buffering in the tray recirculation liquor (very little TDS). In order to keep up the SO_2 removal capacity, it was necessary to operate the system with a neutral or slightly basic pH in the tray loop. Because of the lack of buffering in this liquor, the pH of the tray feed frequently drifted up to 11-12 for extended periods. This resulted in CO_2 absorption and precipitation of $CaCO_3$ in the tray loop, forming a scale throughout the tray tower circuit. The amount of scale formed varied with the duration of such excursions. Unfortunately, the formation of the scale was a cumulative effect, since $CaCO_3$ dissolves very slowly at pH's above 6.5. This scale forced shutdowns on two occasions for cleaning of piping, pumps, and valves.

The scale formation on the trays is evidence of the severity of this problem. Only the top tray and radial vane demister showed appreciable deposition of $CaCO_3$. At the conclusion of run 620 there was a 1/2-3/4 inch scale of $CaCO_3$ (calcite with a small amount of aragonite) covering the entire surface of the top tray. This scale increased the tray tower pressure drop. The middle and bottom trays remained relatively clean, except for the inlet side of the middle tray where some $CaCO_3$ deposition occurred. Figures VII-18 and VII-19 show photographs of the top and middle trays, respectively, at the conclusion of the run.

At slightly lower oxidation rates in the scrubber system in run 620B there was more buffering capacity in the tray tower circulation loop due to the higher levels of TOS. This allowed better control of the pH of the liquor fed to the top tray. However, operation at a pH of 8-11 resulted in the precipitation of calcium sulfite. Although no direct scaling was observed after about 100 hours of operation, the presence of these solids indicates a scale potential.

It is apparent from these results that there is a fine line of operating conditions that should be maintained in order to prevent scaling in the scrubber system. Although not tested, the most promising approach may be to operate a dilute mode scrubber at a pH of about 7 and provide sufficient gas/liquid contacting to ensure good SO_2 removal efficiencies. Such an operation may still be difficult to control if there is enough oxidation to reduce TOS levels in the scrubber system to below 0.02M.

Regeneration System Performance

Table VII-12 summarizes the performance of the various reactor systems used in the closed-loop runs. In all runs, with all reactor configurations, lime utilization exceeded 90%. In runs 601 and 602 with holdup times of 2-3 hours, lime utilization was generally 95% or higher. In run 620, with 90 minute holdup times, lime utilization was slightly higher -- typically about 93% of the available $Ca(OH)_2$. The pH of the reactor feed liquor in run 620 was also slightly higher.

The dewatering properties of the solids produced in the closed-loop runs were also quite good as long as TOS levels in the reactor feed liquor were maintained in the range of 0.02 or lower. At TOS levels above 0.03M, as in run 601, the properties of the solids deteriorated markedly due to high reactor operating pH and long holdup times used. In run 601 the total oxidation across the combined scrubber system and oxidation tank amounted to less than 50% of the SO_2 removal because of the low flue-gas oxygen levels and insufficient aeration in the oxidation tank. The solids generated in the reactor system, therefore, were primarily calcium sulfite, and previous work in the concentrated lime mode showed that a high reactor pH (>10) and a long holdup time (>30 minutes) are unfavorable conditions for producing good calcium sulfite solids with a CSTR.

The quality of the solids produced is indicated both by the settling rates of the solids and the filter cake characteristics. In run 601 the cake contained less than 30% insoluble solids and the solids virtually did not settle. Under identical conditions in run 602, except that the TOS in the feed liquor was reduced to less than 0.01M TOS, the quality of the solids improved markedly, as evidenced by the settling data. However,

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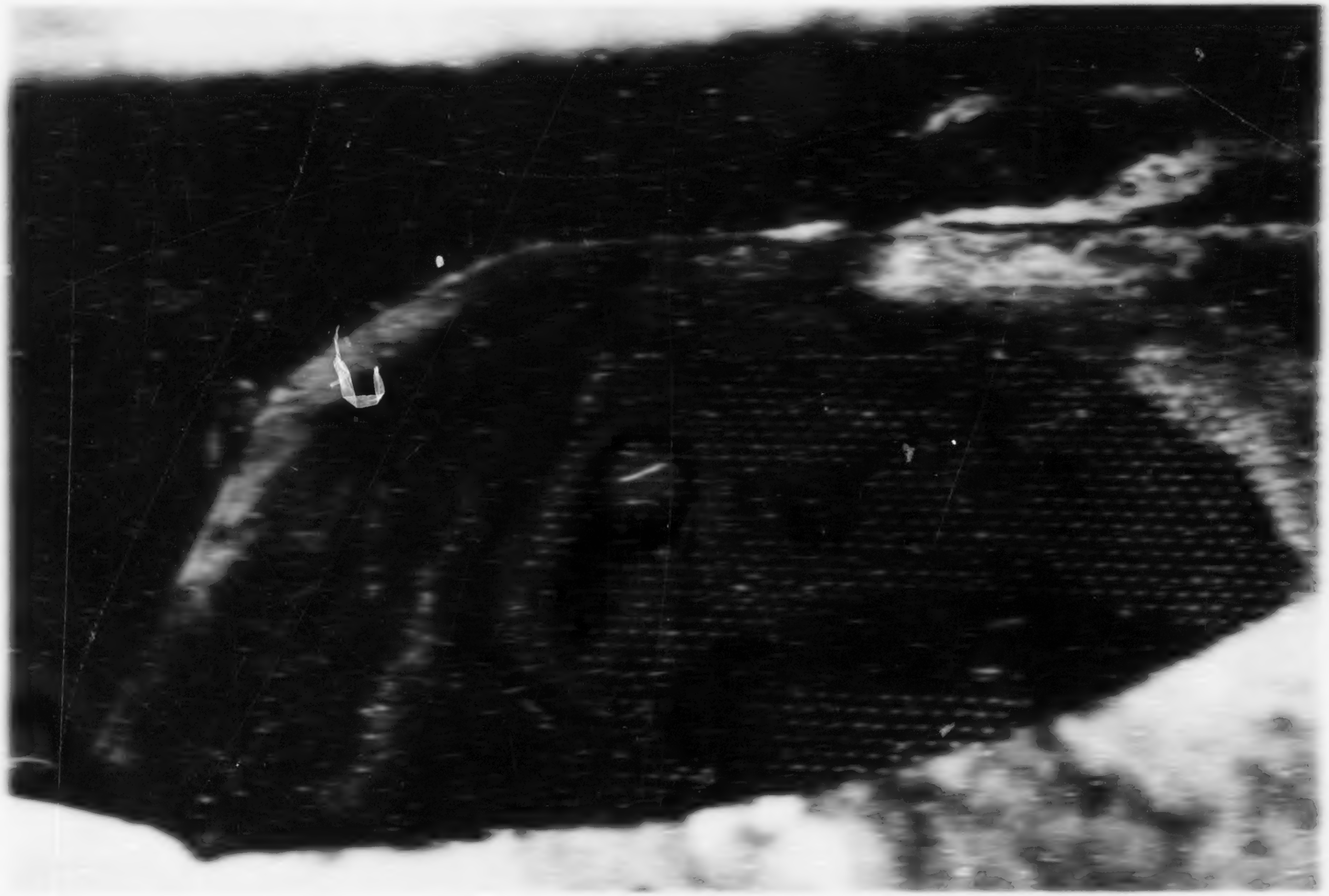

FIGURE VII-[illegible] [illegible]

TABLE VII-12

SUMMARY OF CLOSED-LOOP, REACTOR PERFORMANCE

Run	601	602A	602B	620A	620B
Reactor Parameters:					
Type	CSTR	CSTR	CSTR	CSTR	ADL
Nominal Holdup	2–3 hrs	2–3 hrs	2 hrs	1.5 hrs	1.5 hrs
Solids Recycle	No	No	Yes	Yes	No
Reactor Feed Liquor:					
pH	5.5	5.5–6.6	~5	6–10	7–10
[TOS], (M)	0.05	0.01	0.003	0.002	0.003
$[SO_4^=]$, (M)	0.63	0.53	0.53	0.57	0.51
Reactor Effluent:					
$[OH^-]$, (M)	0.05–0.10	0.095	0.085	0.115	0.09
$[Ca^{++}]$, (M)	0.018–0.024	0.0200	0.0170	0.0178	0.0186
$[Ca^{++}]$, (ppm)	720–960	800	680	710	745
$[Ca^{++}]$ Supersaturation, (ppm)	20–250	120	0	0	30
% Solids	0.8	0.8	1.5	0.5	0.9
Solids Characteristics:					
Initial Settling Rate, (ft/min.)	Would not	0.36	0.05	0.14	0.3
Settling Parameter, (tons/ft^2 day)	settle	0.15	0.12	0.7	0.34
Density of Settled Solids, (wt% solids)		15	20	55	32
Filter Cake—%Solids	<30	–	–	65–80	65–80
Calcium Utilization	100	95–97	~85	~93	~93

since run 602 was a continuation of run 601, the filter cake was a mixture of solids produced during both runs and, therefore, did not reflect the better dewatering properties.

In both parts of run 620 (with the ADL reactor, and with the CSTR and solids recycle) the solids properties were excellent. The filter cake was consistently higher than 60% solids and frequently ran as high as 75-80% solids. An analysis of the solids produced showed that they were essentially pure gypsum, as were the solids produced in run 602.

The need for solids recycle to prevent calcium supersaturation in the reactor liquid (and scrubber system feed) was clearly indicated by these closed-loop tests. The soluble calcium concentrations measured at the different solids levels in runs 602B and 620A are plotted in Figure VII-20. The results show that in order to achieve saturation (approximately 700 ppm Ca^{++}), the solids level in the reactor slurry must be greater than 4% solids. Unfortunately, it was difficult in the open-loop runs previously discussed to achieve greater than 4% solids without actually closing the loop. Thus, reduction of calcium concentration to the saturation level was never achieved except in the closed-loop tests.

The level of calcium observed using the multistage reactor without solids recycle is also indicated in Figure VII-20 (run 620B). With the ADL reactor, soluble calcium concentrations ran about 770 ppm, or about 50 ppm higher than saturation. This is considerably better than that achieved using a CSTR without solids recycle.

As in the scrubber system, the major process problem in the reactor system was scaling. Throughout both parts of run 620, gypsum scale built up in the reactor bleed piping, and thickener overflow weir and piping. This scaling forced numerous shutdowns to clean and flush piping and equipment.

The scale was probably due to supersaturation of calcium in the reactor effluent. Even when the system was run with solids recycle to the reactor, there were extended periods when the solids level in the reactor slurry was below 4% due either to operation according to a prescribed set point or due to inability to set and maintain the underflow recycle rate accurately. It is possible that had a level of 5% solids or greater been maintained in the reactor slurry, scale formation would have been minimal.

E. CONCLUSIONS

Use of limestone only for the regeneration of solutions in the dilute mode (less than 0.15M active sodium) is not viable. As indicated in Chapter VI, the limestone reaction rate decreases as the ratio of soluble sulfate/sulfite increases in the reactor solutions. At sulfate/sulfite ratios required for adequate sulfate precipitation in the dilute mode, reaction rates are poor resulting in poor limestone utilization and poor solids quality.

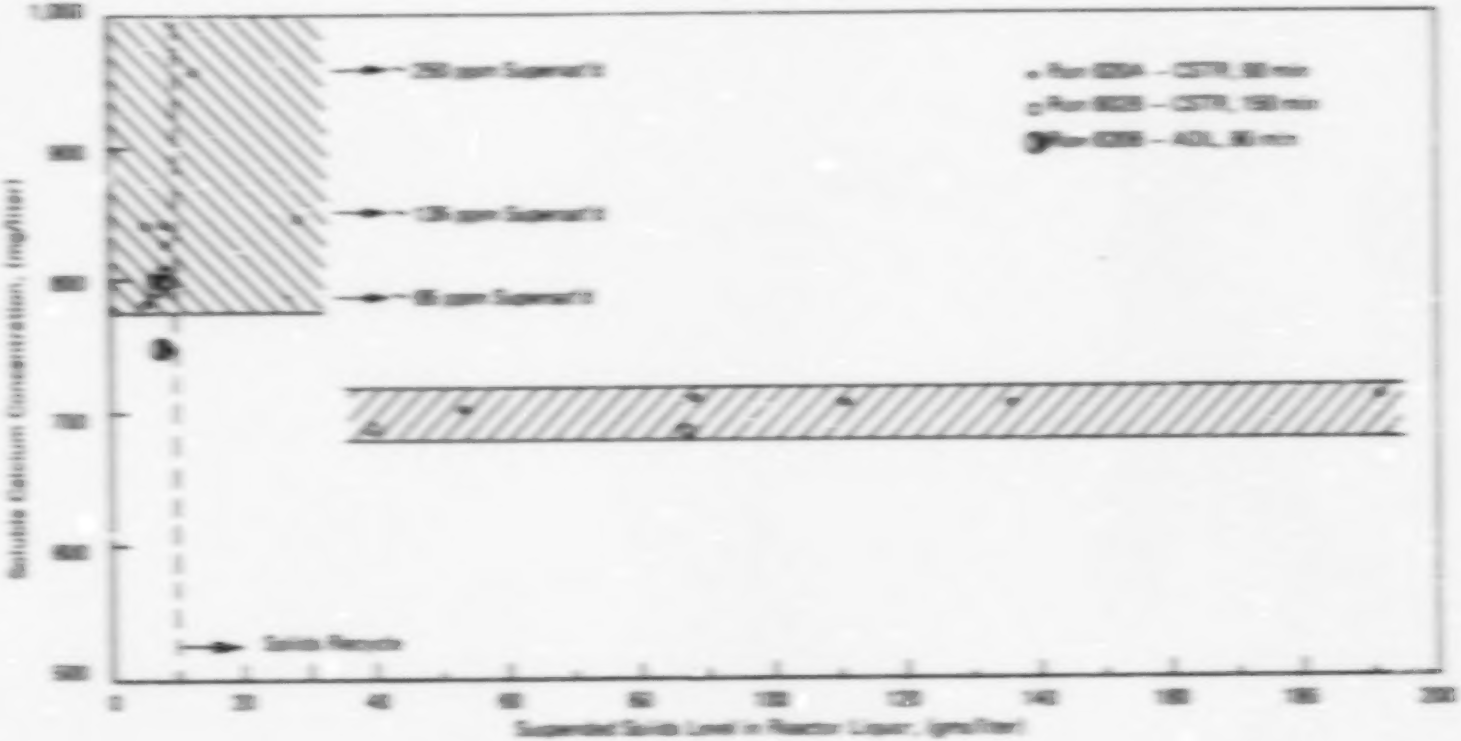

FIGURE VII-28 CALCIUM SUPERSATURATION VS. SUSPENDED SOLIDS LEVELS

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Use of lime in combination with limestone in a dilute dual alkali mode was more viable technically. In this approach, the lime regeneration was carried out in a second reaction system to promote sulfate precipitation. The limestone/lime process is more complicated than a simple dilute lime process, resulting in higher projected capital cost. Economic analysis indicated that operating cost savings which could potentially be realized in using limestone for part of the regeneration would not offset the additional capital cost probably required to enable use of the limestone. The dilute lime system, using soda ash for softening, was technically and economically the most viable dilute mode considered. Conclusions based upon laboratory and pilot plant investigations of this mode are given below.

A dilute lime mode can be operated in a closed loop with sulfate precipitation keeping up with any level of system oxidation. The system can be operated with high SO_2 removal (90% or higher) and good lime utilization (90% or higher) to produce high quality solids (60% insoluble or higher) with low soluble sodium losses (2% achievable). The process may be more appropriate for low-sulfur coal applications or in situations where oxidation rates are expected to exceed 25-30% of the SO_2 removal. The dilute lime mode is somewhat more complicated than the concentrated lime mode, involving higher liquid rates and larger reactors and associated equipment. The process is also potentially less reliable than the concentrated lime approach.

The regeneration reaction, carried out at low sulfite levels, results in the precipitation of calcium sulfate (usually gypsum) to produce a regenerated solution of sodium hydroxide and sodium sulfate with soluble calcium levels which are, at best, at the saturation level of about 700 ppm Ca^{++}. Even with moderate amounts of soda ash makeup (and resulting softening by precipitation of calcium carbonate) the solutions have soluble calcium levels in the range of 600-700 ppm with a high potential for scaling in the system. Close control of scrubber pH is required to prevent carbonate or sulfite scaling. High scrubber oxidation rates may create sulfate scaling.

In the dilute mode regeneration reaction, there is a high tendency to produce solutions which are supersaturated in Ca^{++} (with respect to gypsum). Using a single-stage CSTR with no solids recycle, calcium supersaturation levels of 100-200 ppm are easily encountered. Special design precautions must be taken to prevent supersaturation and the resulting scaling throughout the system. Supersaturation can be reduced in a number of ways, by reactor system design and by controlling conditions of the regeneration reaction:

- Increased reactor residence time -- Allows time for completion of reaction and desupersaturation. Holdup time of 60 minutes is a minimum; 90 minutes is preferable.

- Solids recycle -- Increases suspended solids concentration and seed concentration for reaction and desupersaturation. Recycle of solids to achieve a concentration of 4% or higher suspended calcium salt solids is required to eliminate supersaturation in the reactor effluent.

- Oxidation of sulfite in scrubber bleed prior to regeneration -- Lowers the concentration of TOS which tends to retard the lime/sulfate reaction when TOS is present in the dilute mode concentration range. Oxidation to TOS concentrations of about 0.02M or lower is desirable.

- Multistage reactor configuration -- Solids generated in a short residence time first stage provide good seeds for completion of reaction in longer residence second stage. Using a multistage reactor can reduce supersaturation to within about 50 ppm of the saturation level. Solids recycle is required to completely eliminate supersaturation.

Elimination of supersaturation was achieved in the single-stage reactor, with 90 minutes residence time, using solids recycle to the minimum of 4% suspended calcium salts in the reactor, and with oxidation of the reactor feed solution to TOS levels of 0.02M or lower. Variation in soluble sulfate concentrations in the range of 0.5-0.75M had no apparent effect on the level of supersaturation.

Utilizing these design factors in a dilute mode with lime regeneration not only reduces or eliminates supersaturation, but also promotes a good reaction rate which generally improves the overall process performance parameters such as lime utilization, sulfate precipitation and solids properties. More specifically, the performance of the dilute lime mode relative to the important process performance characteristics is given below:

- SO_2 removal -- SO_2 removal of 90% is easily achieved especially at low to medium inlet SO_2 levels. SO_2 removal is not as efficient as in a concentrated dual alkali mode (with the same scrubber configuration) because of the low active sodium concentration. The scrubber operation is more difficult to control due to the low buffering capacity of the dilute mode liquors. Higher calcium concentrations (in the range of 600-700 ppm Ca^{++}) present potential scaling problems in the scrubbing system. Operation of the scrubber in a high pH range (9-11) to promote good SO_2 removal results in some CO_2 absorption and potential carbonate scale formation. Increasing active sodium concentrations to provide more buffering can result in sulfite scale formation in the pH range of 8-11.

- Lime utilization -- Lime utilization of 90% or higher is achievable when regenerating to hydroxide concentrations of about 0.1M with solutions containing sulfate in the range of 0.5-0.75M and using reactors with a minimum total holdup time of 60 minutes. Utilization increases as the residence time and sulfate concentration are increased. Solids recycle also helps increase lime utilization. However, TOS levels in the feed to the reactor should be

0.02M or less (by deliberate oxidation if necessary) to prevent retarding of the reaction rate by the sulfite.

- Oxidation/sulfate control -- Complete sulfate control is possible in this mode of operation at any rate of oxidation in the system. However, at very high scrubber oxidation rates, sulfite/bisulfite buffering is minimal and scrubber pH control becomes difficult. All other aspects of the process operation are improved by high oxidation rates (i.e., minimal TOS concentration in the feed to the regeneration reactor). Deliberate oxidation should be used to maintain TOS levels below about 0.02M. At sulfate concentration in the range of 0.5-0.75M, calcium sulfate (usually gypsum) is produced instead of a mixed calcium sulfite/calcium sulfate crystal when TOS is maintained at or below 0.02M. At this point, the calcium sulfate content of the solids is no longer limited by the apparent maximum content of 25-30% in the mixed crystal; 100% calcium sulfate can be produced.

- Solids properties -- It is possible to produce excellent quality solids containing 60-80% insoluble solids. Good solids properties are favored by the following conditions:

  - Low TOS in the reactor feed -- less than 0.02M.

  - High sulfate in the reactor feed -- 0.5-0.75M (high end of range favored).

  - Solids recycle -- improves solids quality but increases the solids load and ultimately the size of the thickener.

  - Multistage reactor system -- improves solids quality compared to same total residence time in a single stage.

  - High reactor residence time -- 80% insolubles solids can be produced using a 90 minute residence time reactor.

- Sodium losses -- In any application, increasing the insoluble solids content of the filter cake increases the effective number of displacement washes for any given amount of wash water available. By producing 75% insolubles solids in a high-sulfur coal application, roughly five displacement washes are available (as opposed to two and one-half displacement washes at 50% solids) permitting more effective cake washing; in low-sulfur coal applications even more wash water can be available. Consequently, sufficient wash water should be available to reduce the solubles content of the cake to under 2%, and down to the range of 0.5-1.5% solubles in low-sulfur coal applications. In such applications it may be possible to wash the filter cake to loss levels lower than those corresponding to sodium carbonate makeup levels required for softening of the regenerated liquor. A sodium carbonate makeup rate of 2-2.5% of the SO_2 removal rate provides sufficient carbonate to reduce the Ca^{++} concentration in the regenerated liquor by about 30 ppm, providing only minimum softening. Thus, sodium makeup (and ultimately the losses in the cake) may be controlled by softening requirements rather than by wash water availability or cake washability.

- System operability/reliability -- The dilute lime mode is inherently less reliable and more difficult to control than the concentrated lime mode. When appropriate care is taken to eliminate supersaturation, the calcium levels in the regenerated solution are in the range of 700 ppm. Only a minimum of softening is provided at low sodium carbonate makeup levels. Potential for scaling exists in the reactor system and associated auxiliaries and piping, and in the absorber. Absorber operation is less effective and more difficult to control than in the concentrated mode.

VIII. STUDIES OF THE PHYSICAL PROPERTIES OF DUAL ALKALI PRODUCT SOLIDS

A. INTRODUCTION

In the preceding chapters of this report, several viable dual alkali operating modes were discussed. An important requirement for a dual alkali process is that the solids which are produced have good dewatering properties so that a tight liquor loop can be maintained. If the product solids can be consistently dewatered to a sufficient degree, it might be possible to dispose of them in a reclaimable landfill instead of in a conventional sludge pond. Consequently, as a first step in assessing that possibility, a series of laboratory tests, which are normally used to characterize the behavior of soils in fills and embankments, were applied to samples of dual alkali product solids -- one high in calcium sulfite and the other predominantly gypsum. The behavior of a sample of solids from a direct limestone slurry system was compared to the dual alkali solids in some of the tests.

The principal physical characteristic studied was the behavior of compacted product solids when a load was applied to them. The permeability of the compacted material to water and the concentration of soluble substances in samples of leachate were also determined. Because there has been a good deal of discussion about the possible use of "chemical treatment" to improve the physical properties of FGD sludges, e.g., to increase their load-bearing strength and to decrease permeability, the changes in the properties of dual alkali product solids when they are treated by mixing them with fly ash and either lime or portland cement were studied. Measurements of load-bearing strength, permeability, and leachate composition were made to characterize the efficacy of such treatment.

B. CHEMICAL AND PHYSICAL CHARACTERISTICS

1. Chemical Composition

The results of chemical analyses of each of the three materials studied are shown in Table VIII-1. The sample of high calcium sulfite dual alkali product solids, which will hereafter be referred to as "dual alkali sulfite", was obtained during July 1975 from the CEA/ADL dual alkali prototype system at the Gulf Power, Scholz Steam Plant located in Sneads, Florida. It was composed of about 75% by weight $CaSO_3 \cdot 1/2H_2O$, 15% to 20% calcium sulfate, about 3.5% inert material and essentially no fly ash. Examination of the dual alkali sulfite material by X-ray diffraction (XRD) indicated that only a trace of gypsum was present. It is quite likely that the trace of gypsum detected by XRD resulted from oxidation of calcium sulfite during handling and storage of the material. In a parallel XRD study conducted for Southern Company Services by IU Conversion Systems (IUCS),[2] no gypsum could be detected in a sample of dual alkali sulfite obtained from the same process.

TABLE VIII-1

CHEMICAL COMPOSITION OF FGD PRODUCT SOLIDS

Material	Wt. Percent Acid Insolubles	Chemical Composition (mmoles/g)						
		Ca^{++}	TOS[a]	$SO_4^{=}$	Na^{+}	Mg^{++}	Cl^{-}	OH^{-}
Dual Alkali Sulfite	3.5	7.44	5.12	1.20	0.32	0.14	0.025	n.a.[b]
Dual Alkali Gypsum	nil	n.a.	<0.01	n.a.	0.13	n.a.	n.a.	0.38
Direct Limestone Sulfite	25	6.48	3.04	0.64	0.03	0.07	0.06	n.a.

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[a] Total Oxidizable Sulfur, calculated as sulfite.

[b] n.a.; not analyzed.

In the XRD studies of dual alkali sulfite materials carried out during this program, the diffraction patterns of a number of solids composed primarily of calcium sulfite, but also containing varying amounts of calcium sulfate, were examined with a great deal of care. The sulfite/sulfate mixtures contained no lines to indicate the presence of a calcium/sulfur solid phase other than $CaSO_3 \cdot 1/2H_2O$. That, plus the fact that the $CaSO_4/CaSO_3$ ratio was found to vary when the $SO_4^=/SO_3^=$ concentration ratio in the process liquor was changed, suggested very strongly that the $CaSO_4$ was present as a solid solution within the $CaSO_3 \cdot 1/2H_2O$ crystal. Lattice mismatch must have been small because no evidence of a change in lattice parameters with $CaSO_4$ content could be detected.

The "dual alkali gypsum" was essentially pure gypsum, $CaSO_4 \cdot 2H_2O$, on the basis of both X-ray diffraction and wet chemical measurements. It contained a small amount of unreacted lime, but no TOS could be detected. The material was produced during run 620 in the ADL pilot plant in which dilute mode operation, with intentional sulfite oxidation prior to regeneration, was studied.

The direct limestone FGD sludge, which will be called "direct limestone sulfite", was a sample obtained on June 17, 1975, from the EPA test facility at the Shawnee Steam Plant, Paducah, Kentucky. Calcium sulfite and a small amount of unreacted limestone were the only solid phases which could be detected in that material by X-ray diffraction. It contained about 25 wt % acid insoluble material, the bulk of which was fly ash which is not crystalline and is not detected by X-ray diffraction.

2. Crystalline Morphology

The three product solids chosen for characterization were first examined under the scanning electron microscope (SEM) to observe the detailed morphology of the individual solid particles. As can be seen in the SEM photomicrographs reproduced in Figures VIII-1 and VIII-2, the two dual alkali materials were very different physically. Both of the photomicrographs were taken at a magnification of 950X. The dual alkali sulfite shown in Figure VIII-1 was composed of agglomerates of small, thin needles which are typical of the agglomerates which are found in high calcium sulfite dual alkali solids that settle and filter well. Although the ultimate crystallites which make up each agglomerate were quite small, the agglomerates themselves were reasonably large -- ranging from 10-20 μm in diameter.

The dual alkali gypsum crystals shown in Figure VIII-2, on the other hand, were large, well formed rectangular single crystals about 50 μm in length. In addition to being long and quite wide, the dual alkali gypsum crystals were 3-4 μm thick.

The direct limestone sulfite solids exhibited another distinctly different morphology as the photomicrograph in Figure VIII-3 shows. The magnification in that photomicrograph was 1000X, which is close enough to the magnification used in the other two cases to permit direct comparisons. The

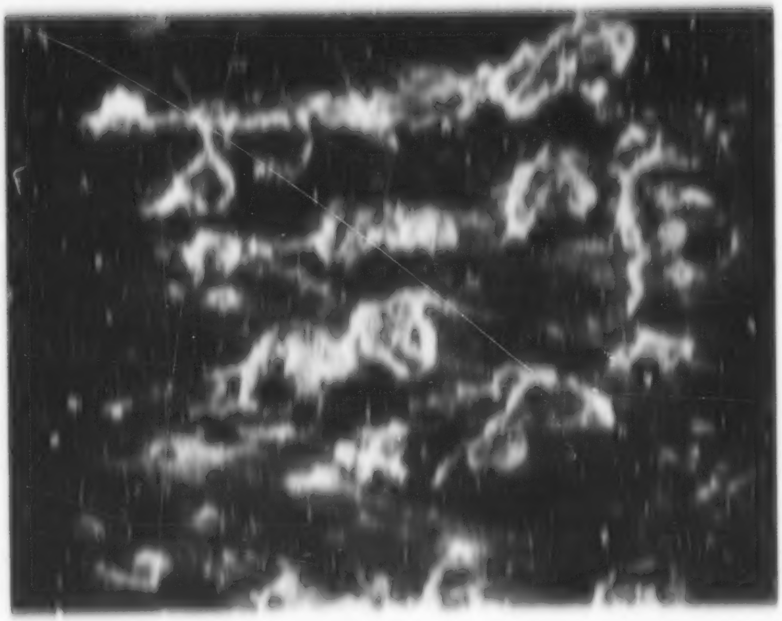


FIGURE VIII-1 DUAL ALKALI CALCIUM SULFITE SOLIDS ([illegible]X)

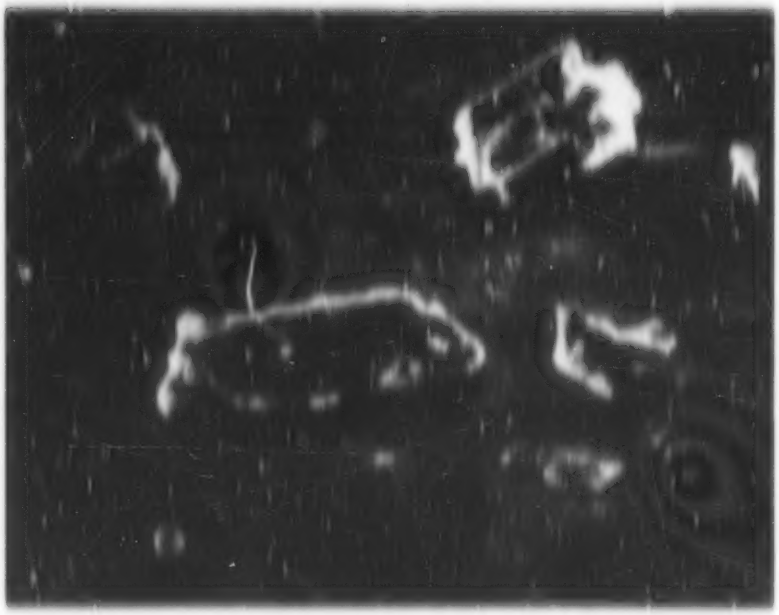


FIGURE VIII-2 DUAL ALKALI GYPSUM SOLIDS (980X)

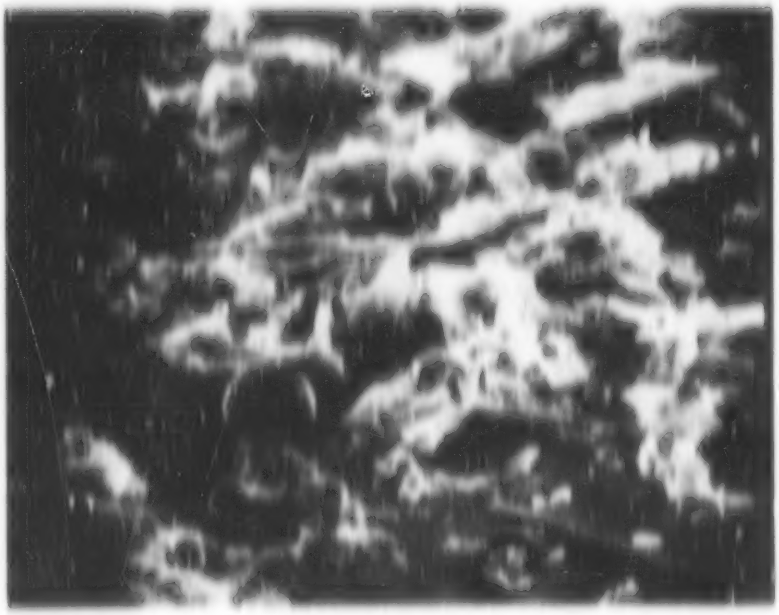


FIGURE VIII-3 DIRECT LIMESTONE CALCIUM SULFITE SOLIDS (1000X)

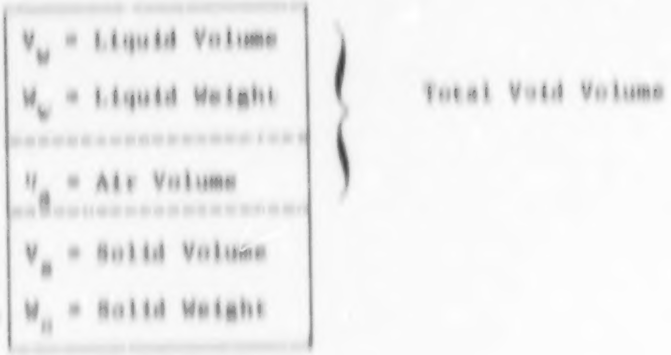
direct limestone sulfite crystals appear to be quite regular rectangles that are not agglomerated. Some were only 2-3 µm long, while others were nearly as long as gypsum crystals. A key characteristic that set the direct limestone sulfite crystals apart from the dual alkali solids was the fact that they were individual crystals (not agglomerated) and were very flat and thin -- only a few tenths µm thick. The spheres in Figure VIII-3 were particles of fly ash which were collected along with the SO_2 in the direct limestone scrubber.

3. True and Apparent Densities of the Solids

As shown in the diagram in Figure VIII-4, the solids are composed of as many as three distinct phases -- the solids, entrained liquor, and entrained air. The actual bulk density of the product solids as they emerge from the process depends upon the proportion of each phase which is present along with the true densities of the solid and liquid phases. The true densities of the solids which made up the samples studied in this work were measured with an air pycnometer and the results are shown in Table VIII-2. Gypsum is less dense than $CaSO_3 \cdot 1/2H_2O$; however, if it is dried at too high a temperature, the gypsum ($CaSO_4 \cdot 2H_2O$) is converted to plaster of Paris ($CaSO_4 \cdot 1/2H_2O$), which has a higher density.

Using the definition of bulk density shown in Figure VIII-4, a typical dual alkali sulfite filter cake composed of 60 wt % solids and 40 wt % diluted liquor would have a bulk density of about 1.6 g/cc or about 100 lb/cu ft. In addition to the definitions of true density, bulk density, and dry bulk density, four other parameters which are useful in characterizing FGD product solids are defined in Figure VIII-4. Weight percent solids, the percentage of the total sample weight which is due to the solid phase, is quite straightforward. However, percent moisture content, which is a term used frequently by civil engineers who work in soil mechanics, is computed in a manner which often appears unusual to chemists and chemical engineers. Percent moisture content is defined as the weight of the liquid phase divided by the weight of the solid phase and expressed as a percent. Thus, for materials which have a great deal of liquid phase present, it is possible to have percent moisture contents of 500% or more. Throughout the discussion which follows, we will use the term weight percent solids exclusively when discussing the proportion of a material which is comprised of liquid and that which is solid.

Also included in Figure VIII-4 are definitions of the void ratio, e, and the degree of saturation, S. Both of these parameters are used when discussing the permeability of solid materials. The void ratio is the ratio of the total void volume, the volume through which a permeating liquid or gas can move, to the solid volume through which such movement cannot take place. The degree of saturation is the percentage of the total void volume which is, in fact, occupied by liquid phase.


V_w = Liquid Volume
W_w = Liquid Weight
V_a = Air Volume
V_s = Solid Volume
W_s = Solid Weight
Total Void Volume

ρ = true density = $\frac{W_s}{V_s}$

γ = bulk density = $\frac{W_s + W_w}{V_w + V_a + V_s}$

γ_d = dry bulk density = $\frac{W_s}{V_w + V_a + V_s}$

Weight percent solids = $\frac{W_s}{W_w + W_s} \times 100\%$

Percent moisture content = $\frac{W_w}{W_s} \times 100\%$

e = void ratio = $\frac{V_w + V_a}{V_s}$

S = degree of saturation = $\frac{V_w}{V_w + V_a} \times 100\%$

FIGURE VIII-4 ELEMENTS OF DUAL ALKALI SOLID WASTE

TABLE VIII-7

TRUE DENSITIES OF FGD PRODUCT SOLIDS AND FLY ASH[a]

Sample	True Density (g/cc)
Dual Alkali Sulfite	2.60
Dual Alkali Gypsum (83°C)	2.39
Dual Alkali "Gypsum" (125°C)	2.82
Direct Limestone Sulfite	2.65
Fly Ash	2.11

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[a] All samples dried at 83°C prior to measurement except for the one sample of gypsum which was dried at 125°C.

C. COMPACTABILITY OF THE SOLIDS -- MOISTURE/DENSITY RELATIONSHIP

When soils are compacted with varying amounts of moisture present, it has been found that as the moisture content increases from zero, the dry density of the compacted material (it is dried after compaction but before determining the density) goes through a maximum. Furthermore, the load-bearing strength of the compacted material is usually a maximum at the maximum dry density. This occurs when small to moderate amounts of water are present in the soil and the water is adsorbed as a film on the surface of the individual soil particles. When the material is compacted the water acts as a lubricant, allowing the solid particles to slide easily against one another and to pack more densely. However, when more than the optimum amount of water is present, the excess water occupies space that solid particles could occupy if the water were not there and prevents the solid materials from being compacted to the maximum density.

As a first approximation, if these solids are considered to be similar to soils, then they too should exhibit greatest load-bearing strength when they are compacted at the optimum moisture content required to produce the greatest compacted dry density. Thus, it was deemed appropriate to study the moisture/density relationship for compaction of the three product solids to determine the moisture content that would be required to produce the maximum compacted density and then to compare those density values with typical values for compacted soils.

1. Apparatus and Procedure

Because the density to which a material can be compacted depends on the means of compaction, the key to obtaining meaningful moisture/density relationship data is to compact the material using a standard, reproducible technique. One standard method of compaction which is widely used is called the "Standard Proctor Compaction" test. This test, which was employed with a minor modification, is described in ASTM D 698-70, Standard Methods of Test for Moisture/Density Relations of Soils.

The version of the Proctor Compaction used in this work differed from the standard method primarily in the sample size used. Because the available molds were smaller, the volume of solids used was about one-half that described in the ASTM procedure. However, by making other appropriate changes so that the compactive energy per unit volume was maintained at the standard value of 12,400 ft-lb/cu ft., the results from this work should be directly comparable to those obtained with the standard tests.

The sample mold used was a plastic cylinder (2.7 in. diam., 4.6 in. high) fastened to the laboratory bench. A 2.8 lb rammer was then positioned 12 in. above the solid surface in a guide sleeve. The weight was allowed to fall freely 25 times, with the blows evenly distributed over the surface; each sample was made up of three layers with the procedure described above repeated on each layer. After compaction, the sample was weighed and the moisture content determined.

Preparation of the material to be compacted was an important part of the test. Following the standard procedure used for soil studies, the filter cake was first oven-dried at about 83°C until the solid was completely dry. An appropriate amount of dry material was then weighed out and water was added to obtain a particular desired nominal moisture content. The soil-water mixture was then allowed to stand in a covered container overnight to ensure that the entire mixture was homogeneous. By varying the water added, it was possible to obtain a complete curve of dry density versus percent moisture content. This method of sample preparation was used in all physical testing.

2. Results and Discussion

The results of the Proctor compaction tests which were carried out on samples of the three product solids are shown in Figure VIII-5. For both the dual alkali sulfite and the dual alkali gypsum materials, the dry density of the compacted sample passed through a maximum when the material being compacted contained about 75 wt % solids. The position of the maximum for the dual alkali sulfite was quite well defined. However, with only three data points available for the dual alkali gypsum material, it was not possible to define the maximum with the same degree of certainty. It is possible that the actual maximum lay at a slightly higher weight percent solids and the corresponding dry density might have been somewhat higher than the 77 lbs/cu ft. that was measured at 75 wt % solids. However, regardless of this uncertainty, the dual alkali gypsum could be compacted to a significantly higher density than could the dual alkali sulfite, even though the true density of the dual alkali gypsum crystals was about 8% less than that of the dual alkali sulfite solids.

The lower compacted density observed for the dual alkali sulfite is a likely result of the significant difference in morphology of the two materials (compare Figures VIII-1 and VIII-2). The agglomerates of small crystallites that comprise the dual alkali sulfite solids contain a good deal of void space which is responsible for the good dewaterability and washability of the material. Unless the void space was eliminated by fracturing the agglomerate during compaction, however, it would lead to a lower compacted density. The dual alkali gypsum crystals, on the other hand, are quite regular and could align themselves into a rather dense mass upon compaction. For comparison, one sample of the direct limestone sulfite material was compacted at 75 wt % solids. With only one data point, it is obviously impossible to determine if the density of 79 lbs/cu ft. was the maximum dry density which could have been attained.

For reference, a silty clay soil can typically be compacted to a maximum density of about 100 lbs/cu ft. if compaction is carried out at about 83% solids. Although compactability alone is not a sufficient criterion for judging disposal acceptability, the FGD product solids were compactable to dry densities not drastically different from silty clay, and the latter is quite amenable to inclusion in landfill operations.

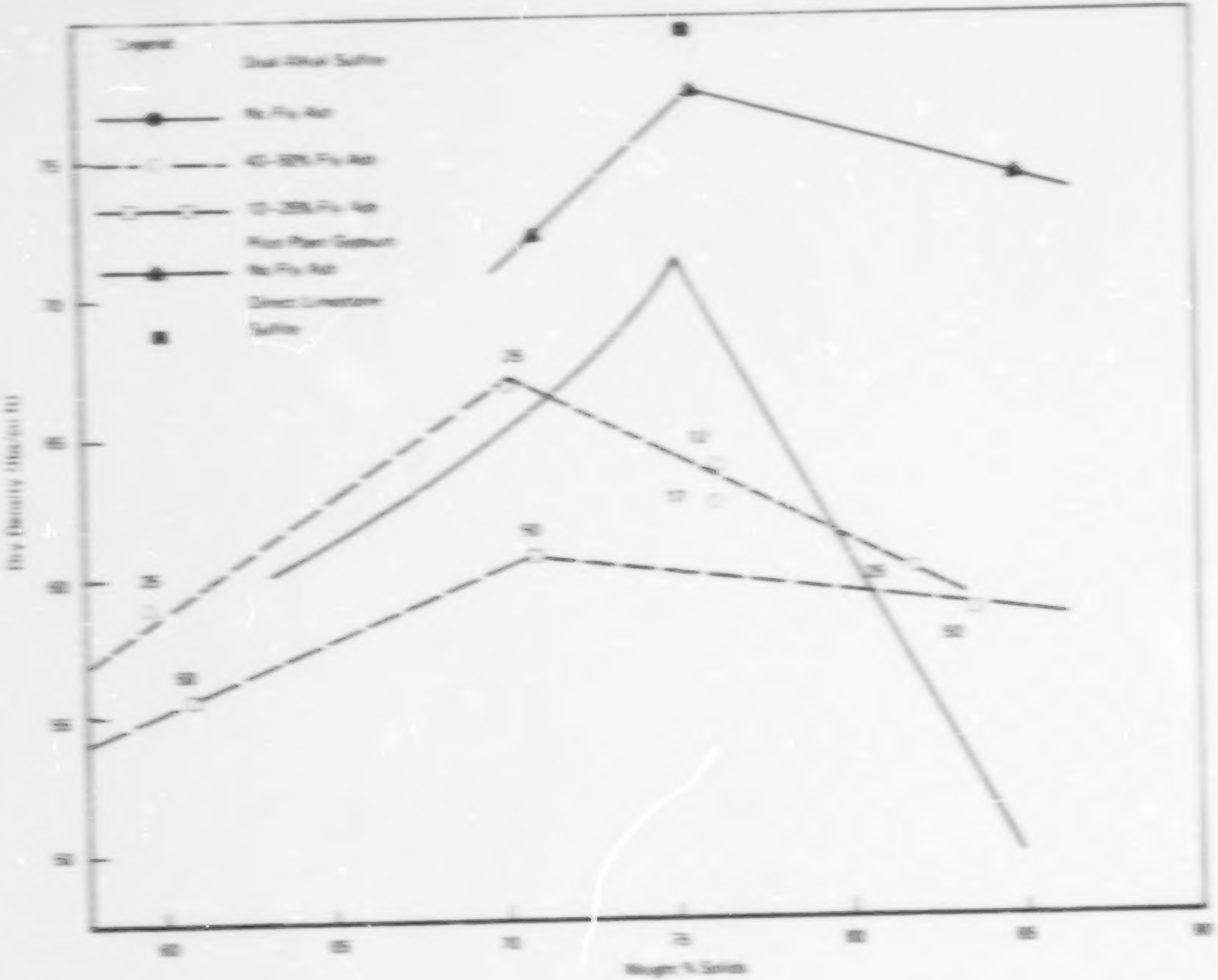

FIGURE VIII-5 COMPACTION OF DUAL ALKALI PRODUCT SOLIDS

For the dual alkali sulfite material, some additional dewatering over and above that which can be produced by vacuum filtration would be necessary to reach the moisture content where maximum compacted dry density can be achieved. One means of increasing the solids content above that which can be produced by filtration is to add dry fly ash to the filtered material. The effect of fly ash addition on the moisture/density relationship for the dual alkali sulfite sample was studied at two levels of added fly ash and the resulting moisture/density curves are shown by the broken lines in Figure VIII-5. For mixtures composed of dual alkali sulfite and fly ash, the weight percent fly ash present in the sample (dry basis) is indicated by the circled number next to each data point.

The addition of fly ash had two distinct effects on the moisture/density relationship. It shifted the optimum weight percent solids to a lower value and it resulted in a decrease in the maximum compacted dry density which could be achieved. The reduction in compacted dry density was not completely unexpected, since fly ash is considerably less dense than dual alkali sulfite -- 2.11 g/cc versus 2.60 g/cc. In fact the maximum dry densities measured for the mixtures containing 25 wt % (dry basis) and 50 wt % (dry basis) fly ash are very close to the densities one would predict by adjusting the maximum dry density of solids without fly ash, for the amount of fly ash added.

Although the preceding studies showed that if they were dewatered sufficiently well, dual alkali solids could be compacted, an important question remained. What might happen if solids were dumped and compacted and then, at a later time, saturated with water? Might they reslurry and become plastic? Table VIII-3 shows the changes which occurred when three samples of dual alkali sulfite solids were stored under water for two weeks after being saturated by evacuating air and pulling water through.

The compacted sample was prepared by the Proctor method and the molded sample was prepared by randomly pushing a glass rod into the solid to release trapped air; the uncompacted sample was merely placed in a sample cylinder and left untouched. The compacted and rodded samples showed no observable change in total volume after saturation and soaking, indicating that the void ratio remained constant. However, there was a noticeable increase in the degree of saturation as more air voids were filled with water during the saturation process and soaking period. Of most significance was the observation that the compacted sample, which had a hard surface prior to soaking, did not swell or reslurry during the period of soaking.

D. RESISTANCE OF THE SOLIDS TO PHYSICAL PENETRATION

One result of a search for test procedures to characterize the load-bearing strengths of the solids, particularly after they were compacted, was a technique called penetrometry. In that technique, one measures the load required to force a blunt probe of a relatively small diameter into a test specimen at a constant rate.

TABLE VIII-3

WATER STABILITY TESTS ON DUAL ALKALI SULFITE

Sample	Final Dry Density After Soaking (lbs/cu. ft.)	Volume Change (%)	Degree of Saturation[a] Initial (%)	Degree of Saturation[a] Final (%)	Appearance After Soaking
Compacted	65	0	69	85	Hard dry surface, no observable change in characteristics.
Rodded	47	0	42	71	Firm moist surface, not pourable, sample slid from mold intact.
Uncompacted	46	-25	41	70	Soft wet surface, fairly dense, not pourable, but surface deforms upon changing position.

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[a] See Figure VIII-4.

1. Apparatus and Procedure

Penetration tests were carried out according to ASTM method D 1558-71, Standard Method of Test for Moisture-Penetration Resistance Relations of Fine-Grained Soils. The tests were carried out using an Instron Universal Testing Machine (Model TTD), equipped with a needle having a diameter of 5/16 in. The samples to be tested were contained in cylindrical plastic molds 2 5/8 in. in diameter. The experiments were performed at two constant penetration rates: (1) 20 in./min -- a relatively rapid rate similar to that used in field measurements of penetration resistance, and (2) 2 in./min -- a slower rate to simulate more closely a static loading.

2. Results and Discussion

The general shape of the load-penetration curves obtained is shown in Figure VIII-6. The yield load is the point at which the needle requires maximum force to overcome the initial solid resistance. It is the yield load which is of value in comparing the resistance of materials to penetration. After yield, the load drops off until it reaches a minimum termed the compaction load, and then, due to the limited height of the samples, there is an increase again in load with further penetration.

Loads and penetrations at yield for five differently treated samples of dual alkali sulfite solids are shown in Table VIII-4. As would be expected, the yield load was greater at the higher penetration rate. Samples 1 and 2, which had been compacted by the Proctor method, had significantly greater penetration resistances than the three uncompacted samples. The lubricating effect of water produced the lower yield loads for sample 2 compared to sample 1, even though they had similar dry densities. Comparison of sample 1 with samples 3 and 4 -- all at about the same saturation -- shows the effect of dry density. The higher density produced by compaction resulted in a substantial increase in yield load. Sample 5, which was uncompacted, unsaturated, as-received material, had an anomalous load/penetration curve. No maxima or minima in the load curve were observed; rather, load increased monotonically with penetration distance.

The yield loads shown in Table VIII-4 are plotted as a function of weight percent solids in Figure VIII-7. For comparison, the dry densities after standard Proctor compaction were taken from Figure VIII-5 and included in Figure VIII-7. At less than the optimum percent solids, both dry density and yield load increase with decreasing moisture content. Shown in Figure VIII-8 are similar curves from the literature for a clay soil (reversed since the abscissa is moisture content). (Ref. VIII-2.) The curves are similar in shape, but the optimum moisture content for the clay (≈20%) was lower than for the dual alkali sulfite solid (≈33%). In the vicinity of the optimum moisture content, both substances exhibited significant resistance to penetration. The clay usually requires a load of 400-800 psi for

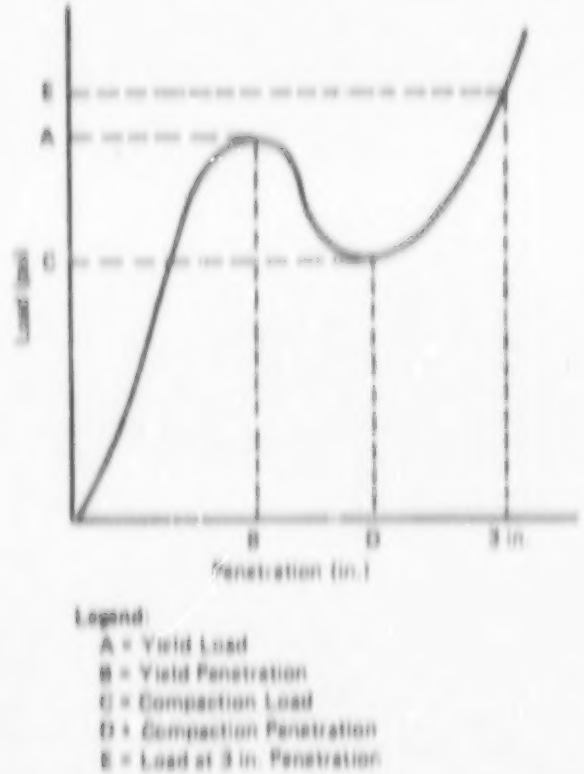

FIGURE VIII-6 LOAD VS. PENETRATION OF DUAL ALKALI SULFITE SOLIDS

TABLE VIII-4. PENETRATION TESTS OF DUAL ALKALI SULFITE SOLIDS

Sample[a]	Degree of Saturation %	Speed of Penetration (in/min.)[b]	Yield Load (psi)	Yield Penetration (in.)	Yield Penetration (% Sample Height)
1. Compacted to 64 lbs/cu.ft. Unsaturated	67	20	860	1.50	35
		2	717	1.25	29
2. Compacted to 65 lbs/cu.ft. Saturated	85	20	535	1.00	24
		2	456	1.00	24
3. Rodded to 47 lbs/cu.ft. Saturated	71	20	70	0.25	6
		2	33	0.25	6
4. Uncompacted 46 lbs/cu.ft. Saturated	70	20	52	0.10	2
		2	33	0.10	2
5. Uncompacted 37 lbs/cu.ft. Unsaturated	33	20	ND[c]	ND	—
		2	ND[c]	ND	—

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[a] Sample height was approximately 4.25".

[b] Penetration needle diameter, 5/16"; area, 0.0767 sq. in.

[c] A maximum in load indicating the point of yield was not detectable.

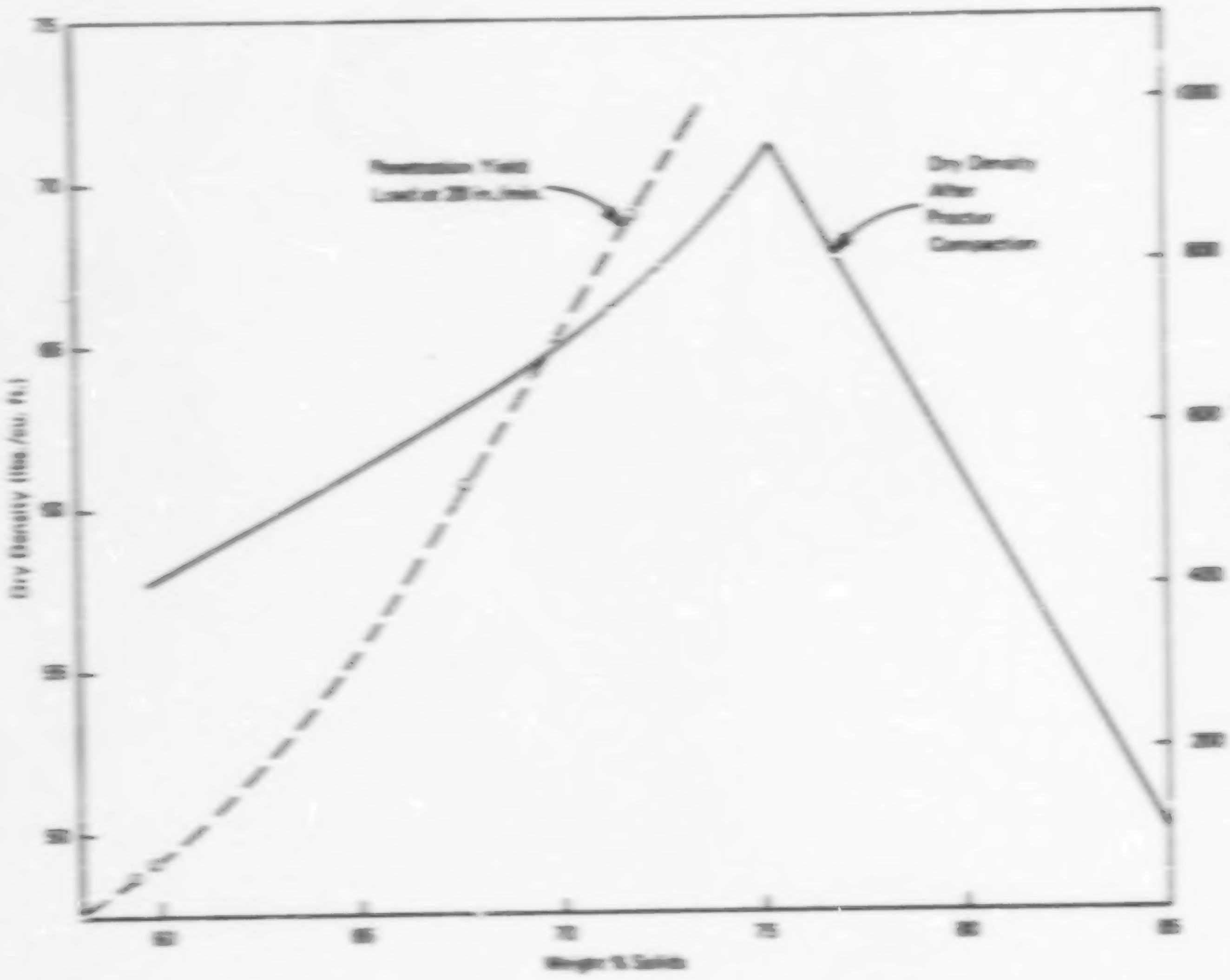

FIGURE VIII-7 PENETRATION RESISTANCE OF DUAL ALKALI SULFITE SOLIDS

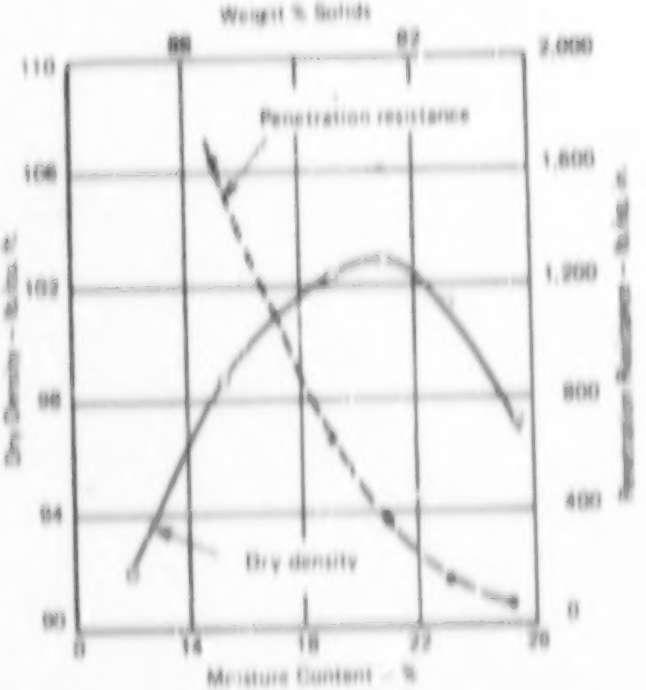

FIGURE VIII-6 RELATIONSHIP BETWEEN PENETRATION RESISTANCE OF A PROCTOR NEEDLE AND MOISTURE CONTENT OF A CLAY SOIL COMPARED WITH DRY DENSITY/MOISTURE CONTENT CURVE

penetration. The compacted dual alkali sulfite sample had a yield load of about 800 psi at a weight percent solids less than the optimum, and the yield load seemed to be increasing in the same fashion as the one in Figure VIII-8. Thus, from standpoint of penetration resistance, the compacted dual alkali sulfite material performed as well as, or better than, the clay.

E. UNCONFINED COMPRESSIVE STRENGTHS OF COMPACTED DUAL ALKALI SOLIDS

Although the technique is usually reserved for "stronger" materials like concrete, unconfined compression tests can be performed on soil-like materials. Triaxial compression tests are more appropriate for studying soil-like materials; however, access to the necessary equipment was not available within the time and budget constraints of this program. Since the apparatus for unconfined compression tests war readily available, measurements on compacted dual alkali sulfite and dual alkali gypsum were carried out.

1. Apparatus and Procedure

Samples were prepared for unconfined compression tests by compacting them in cylindrical molds by the Proctor compaction technique described earlier (Section C-1). They were compacted at approximately the optimum weight percent solids at which maximum dry density could be achieved.

After they were compacted, the molds were removed and the samples tested on an Instron Testing Machine (Model TTD) according to ASTM Method D 1633-63. The samples were compressed at a constant speed of 0.04 in./min until they fractured.

2. Results and Discussion

The unconfined compressive strength of a sample is the stress (force/unit area) which is being exerted at the onset of failure. Since the compacted dual alkali solids were not hard or brittle, failure did not occur catastrophically; rather, failure was observed as a slow decrease in stress at a constant loading rate. The decrease in stress was accompanied by cracking and subsequent fracture of portions of the specimen.

The stress at failure observed for the two dual alkali solids is shown in Table VIII-5. The unconfined compressive strengths of 10 psi and 15 psi are quite low in comparison to those of "strong" materials like concrete which have unconfined compressive strengths in the range of thousands of psi. However, an unconfined compressive strength of 10-15 psi compared quite closely to that of many natural solids.

F. PERMEABILITIES OF SOLIDS

If these solids are to be disposed of in a landfill operation, the permeability of the disposed mass to groundwater or surface water can be an important factor in the impact which the landfill operation has on the

TABLE VIII-3

UNCONFINED COMPRESSIVE STRENGTHS OF COMPACTED DUAL ALKALI SOLIDS

Sample	% Solids	Dry Density (lbs/cu ft.)	Test Specimen		At Failure	
			Diam. (in.)	Height (in.)	Stress (psi)	Strain (in.)
Dual Alkali Sulfite	73.7	67.6	2.69	5.25	25	0.019
Dual Alkali Gypsum	75.6	77.3	2.69	5.63	10	0.045

groundwater in the immediate vicinity. If the permeability of the material being disposed can be reduced, then although the concentration of soluble substances in the leachate leaving the disposal area may not have changed, the rate of pollutant discharge would be reduced in proportion to the reduction in permeability.

1. Apparatus and Procedure

The permeabilities of FGD product solids were measured using a constant-head permeability apparatus as described in ASTM D 2434-68, Standard Method of Test for Permeability of Granular Soils (Constant Head). All of the samples which were studied were first compacted in cylindrical plastic molds by the standard Proctor method discussed previously. Then tight-fitting end caps with tubulations to which plastic tubing could be attached were sealed to both ends of the molds. Next, the entrained air was evacuated from the samples, and they were saturated with de-aerated, distilled water. Finally, a constant-head water supply was connected to the sample cell and the volume of water which flowed from the bottom of the cell was measured as a function of time.

The coefficient of permeability, k, in units of cm/sec, was then calculated from the formula

$$k = \frac{QL}{thA}$$

where Q = total volume of water measured
L = length of sample
t = elapsed time for volume measurement
h = total head of water
A = cross-sectional area of sample.

2. Results and Discussion

The coefficients of permeability measured for two samples of dual alkali sulfite and one sample each of dual alkali gypsum and direct limestone sulfite are given in Table VIII-6. The dual alkali solids ranged in permeability from 0.2×10^{-4} to 1.0×10^{-4} cm/sec. The dual alkali gypsum had the lowest permeability. The five-fold difference between the permeabilities of the two dual alkali sulfite samples was probably due to the combined effects of a lower compacted dry density (more void volume through which water can pass) and a greater degree of saturation (relatively more of the void volume actually participating in the permeation process) in the second sample.

The range of measured coefficients of permeability for the dual alkali solids is similar to that exhibited by relatively pervious silts. Coarse grained sands would be more permeable. Clays would have lower coefficients of permeability. Some very impervious clays have coefficients of permeability in the range of 10^{-7} to 10^{-8} cm/sec.

TABLE VIII-6

PERMEABILITIES OF COMPACTED FGD SLUDGE SOLIDS

Material	% Solids	Compacted Dry Density (lbs/cu.ft.)	Degree of Saturation (%)	Coefficient of Permeability (x 10^{-6} cm/sec)
Dual Alkali Sulfite	70.0	66.0	70	0.56
Dual Alkali Sulfite	76.7	61.4	79	2.96
Dual Alkali Gypsum	72.0	72.0	74	0.21
Direct Limestone Sulfite	75.0	79.6	95	(n.d.)[a]

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[a] A valid permeability could not be obtained due to permeameter blockage; see text.

A valid measure of the permeability of the direct limestone sulfite sample could not be obtained. When the sample was first installed in the permeameter and saturated with water, it was firm and the flow of water from the permeameter corresponded to a permeability of 0.3 x 10^{-4} cm/sec. However, after it had been in the permeameter for a short time, it showed signs of reslurrying, became quite fluid, and the apparent permeability fell to 0.06 x 10^{-4} cm/sec. That behavior suggested that at the very bottom of the permeation cell, a few layers of the very thin, flat, direct limestone sulfite platelets had oriented themselves one on top of the other, effectively blocking the flow. It is likely that a phenomenon such as that is responsible for the fact that sludges consisting of individual platelets are often very difficult to dewater by vacuum filtration. Certain types of clay which are also composed of very thin, flat platelets are known to be equally difficult to dewater by filtration.

G. LEACHING OF SOLUBLES FROM DUAL ALKALI SOLIDS

Several relatively simple experiments were carried out to study the way the major cations, sodium and calcium, leached from compacted samples of dual alkali sulfite and dual alkali gypsum. The aim of the experiments was to obtain some initial data about the leaching behavior of untreated materials, both for its own sake and for use as baseline data to which the leaching behavior of treated materials could be compared.

1. Apparatus and Procedure

Leaching tests were carried out using compacted samples contained in the same type of cylindrical plastic molds fitted with end caps which were used for the determinations of permeability. De-aerated, distilled water was passed through the solids in the test cylinders and fractions of the leachate were collected for analyses of sodium and calcium by atomic absorption spectrometry.

In one extended test, which was allowed to proceed for a period of 80 hours, the flow of water through the cylinder was controlled at about 0.25 ml/min. The total amount of leachate collected during that period corresponded to about 4.4 times the total void volume of the solids in the test cylinder. Two accelerated leaching tests were carried out at considerably higher flow rates of about 1.7 ml/min for comparison. Leachate equivalent to about three void volumes was collected during each of those tests.

2. Results and Discussion

The concentrations of sodium and calcium in each of the seven leachate fractions which were collected during the extended leach test of dual alkali sulfite are shown in Table VIII-7. Included in the table are estimates of the total dissolved solids (TDS) concentrations, which were arrived at by converting the measured concentrations of sodium and calcium to equivalent concentrations of sulfate salts and summing them. The maximum sodium concentration was found in the first fraction collected, which corresponded to the displacement of about 0.4 void volumes of leachate. In the

TABLE VIII-7

LEACHING OF SODIUM AND CALCIUM FROM UNTREATED DUAL ALKALI PRODUCT SOLIDS

Material	Eluate Fraction	Volume of Fraction (ml)	Cum. Void Volume	[Na$^+$] ppm	[Ca$^+$] ppm	TDS Estimated (ppm)[a]
Dual Alkali Sulfite	1	124	0.42	2,748	496	10,100
	2	248	1.30	2,200	396	8,820
	3	144	1.82	950	552	4,810
	4	276	2.81	540	592	3,680
	5	242	3.32	330	604	4,700
	6	198	4.03	198	604	2,660
	7	112	4.43	120	604	2,420
Dual Alkali Sulfite	1	396	1.56	3,100	520	11,300
	2	312	2.78	600	588	3,890
Dual Alkali Gypsum	1	131	0.51	520	1126	5,430
	2	362	1.93	580	1135	5,720
	3	326	3.17	56	1293	4,360

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[a] Total Dissolved Solids concentration; calculated as the sum of the sodium and calcium concentrations expressed as sulfate salts.

second fraction, which included the remainder of the first void volume displacement and an additional 0.3 of the second displacement, the sodium concentration had fallen to 2,200 ppm. A continued rapid drop in sodium concentration was observed in succeeding fractions. The calcium concentration remained more or less constant at about 600 ppm.

The fact that the calcium concentrations in all of the eluate fractions remained more or less constant while sodium decreased by more than a factor of 20 is probably the result of the presence of a small amount of gypsum in the dual alkali sulfite material which was tested. If one assumes for the sake of simplicity that all of the sodium and calcium in fraction 1 were present as sulfate, the ionic strength of that solution would have been about 0.23M, and the apparent solubility product for calcium sulfate, K_{sp}' (see Chapter IV), would have been about 9×10^{-4}. (The product of the calcium and estimated sulfate concentrations in mols/l.) This apparent solubility product agrees with the value predicted for gypsum in a solution of that ionic strength. The concentration of sodium decreased as the sodium salts, primarily Na_2SO_4, were washed from the sample cylinder. The calcium concentration remained essentially constant, however, because of two counter-balancing changes which occurred. In fraction 7, which had a significantly lower ionic strength (about 0.07M), the apparent solubility product for calcium sulfate had fallen to about 2×10^{-4}, which is not unreasonable. But, since the concentration of sulfate ion had fallen similarly, the calcium level remained relatively constant in accordance with K_{sp}'.

From the standpoint of the pollution potential of the dual alkali sulfite leachate, if one again makes the simplifying assumption that all of the salts were present as sulfates, the total dissolved solids (TDS) in fraction 1 would have been about 10,000 ppm. The leachate at the end of the experiment would have contained about 2,400 ppm TDS. One would expect the concentration of TDS in the leachate to remain constant at about 2,000 ppm as long as gypsum was present in the solid phase. With no gypsum present, and under strictly anaerobic conditions, one would expect the concentration of TDS leachate from calcium sulfite to be a great deal lower -- in the range of 100-200 ppm.

The expectation that TDS levels would be considerably lower when a distinct gypsum phase was not present in the sludge was confirmed by the results of the parallel studies conducted for Southern Company Services by IUCS[7]. When the sample of dual alkali sulfite studied in that work, a material shown to contain $CaSO_4$ but no gypsum, was subjected to five successive batch washes (1 g dry solids per 4 g water), the TDS level in the final wash was 682 ppm. Since it was not stated that those washes were carried out under strictly anaerobic conditions, it is likely that TDS would have been even lower if all oxygen had been excluded.

The dual alkali sulfite solids studied in the extended leaching experiment contained 0.37 mmol/g of sodium. After the extended leaching experiment had been terminated, samples of the leached solids were analyzed and were found to have a sodium content of 0.11 mmol/g, suggesting that only about two-thirds of the total sodium had been leached. When the total sodium measured in each of the seven fractions collected during the leaching experiment was totaled, about 90% of the 0.21 mmol/g of sodium leached, based on the solids analyses, could be accounted for in the leachate.

The extended leaching experiment suggested that a portion of the total sodium in the dual alkali sulfite solids was very difficult to leach. This phenomenon was examined further by performing three batch leaches in which 5-gram samples of dual alkali sulfite solids were stirred in three, 100-ml portions of water for 30 minutes, 60 minutes, and 120 minutes, respectively. After stirring, a portion of each slurry was centrifuged and the supernatant liquid was analyzed for sodium. The concentration of sodium in the supurnatant solutions was independent of stirring time. In each case the amount of sodium found in solution corresponded to 0.19 mmol/g of sodium leached from the calcium sulfite solids. By difference, the leached solids should have contained 0.13 mmol/g sodium, a concentration which agreed quite closely with the 0.11 mmol/g residual sodium found in the solids after the extended column leach test.

The sodium balance observed in both the column and batch leaching experiments indicated that about 30% of the total sodium in the solids was not available for leaching. The most plausible explanation for the unavailability of that sodium is that it was either occluded, or in true solution, within the calcium sulfite/sulfate crystals.

An accelerated leach of dual alkali sulfite in which the eluting water was passed through the column at a ten-fold higher rate than in the extended leach was carried out for comparison. The leachate from that test was collected in two fractions, and the concentrations of sodium and calcium measured in each are included in Table VIII-7. The behavior of the dual alkali sulfite was not appreciably different in the accelerated leach than in the extended test. The sodium concentration in the first fraction was somewhat higher than had been measured in the initial fraction which was collected during the extended leach, but the concentration in the second fraction was comparable to those measured in fractions 3 and 4 of the extended leach, which corresponded to about the same void volume increment. The fact that the concentrations found in the accelerated test were not substantially lower indicate that at the higher flow rate, leaching was not rate limited.

A sample of dual alkali gypsum was also subjected to accelerated leaching at a flow of about 2.7 ml/min. Analyses of the three fractions of leachate which were collected during the test are included in Table VIII-7. The sodium concentrations in the first fractions collected were lower for the dual alkali gypsum than for the dual alkali sulfite, because the gypsum solids initially contained less total sodium (0.13 mmol/g) than did the dual alkali sulfite (0.32 mmol/g). The difference in total sodium content was due to the fact that the gypsum was produced during "dilute mode" operation where total sodium concentrations in the process liquor were lower and more cake washing applied than used for the production of the dual alkali sulfite. An examination of the total amount of sodium collected in the leachate from the gypsum leach test indicated that only about half of the 0.11 mmol/g total amount of sodium initially present had been leached even though the sodium concentration was very low in the last fraction collected. Again, this suggests that sodium might have been entrapped within the gypsum crystals too.

H. EXPLORATORY STUDIES OF THE EFFECTS OF CHEMICAL TREATMENT ON THE PROPERTIES OF DUAL ALKALI SOLIDS

Chemical treatment by addition of lime and fly ash, or one or another proprietary ingredient, has been proposed as a means for improving the physical and chemical properties of FGD sludges to make them better suited for disposal in landfills or in ponds which can ultimately be covered and reclaimed. Most chemical treatment has involved sludges produced by direct slurry scrubbing systems. Since the effectiveness of treatment seems to depend upon arriving at the optimum technique for a particular sludge, it was decided to perform a few initial exploratory studies to determine the improvement, if any, that chemical treatment might impart to the physical and chemical properties of dual alkali solids.

1. Experimental Procedures

The treatment techniques studied involved the addition of fly ash and a source of lime to the solids to be treated. The silica in the fly ash undergoes the well-known pozzolanic reaction with calcium from the lime to produce an insoluble, cementitious calcium silicate matrix which has been shown in other studies to increase the strength of the solids and decrease their permeability. The source of lime was either quicklime (CaO) or portland cement; the latter is a source of both lime and silicate. Treatment consisted of mixing samples of dual alkali sulfite or gypsum with varying proportions of fly ash and CaO or portland cement. A few of the treated mixtures were prepared in an excess of water, poured into molds, allowed to settle, and then left to cure under water. Other mixtures were prepared by mixing the three ingredients in the presence of the required amount of moisture for optimum Proctor compaction as described previously. After compaction, the samples were removed from their molds, placed in a 100% relative humidity chamber at room temperature, and allowed to cure for either 14 or 28 days.

The primary measure of treatment effectiveness was the increase in unconfined compressive strength imparted to the samples by the various treatments. Single samples of treated dual alkali sulfite were also subjected to permeability and leaching tests.

2. Results and Discussion

The unconfined compressive strengths of the various treated dual alkali solids are shown, along with the kinds and amounts of additives used for each, in Table VIII-8. As noted earlier, the actual compressive strength of the sample is the stress at the onset of failure; the strain

TABLE VIII-8

COMPRESSIVE STRENGTH OF DUAL ALKALI SOLIDS
(CURED AT 100% RELATIVE HUMIDITY)[a]

		Sample Composition Prior to Curing					Test Specimen		Curing	Unconfined Compressive		Secant Modulus of Elasticity at Compressive Strength
		Weight %										
Sample	Source of Solids	Fly Ash	Solids[b]	CaO	%Solids	Dry Density (lbs/cu ft.)	Diam. (in.)	Height (in.)	Time (Days)	Stress (psi)	Strain	(psi)
1	Scholz	68.9	24.2	6.9	—	50.8[d]	2.00	7.50	28	86	0.048	1,805
2[c]	Scholz	47.6	33.3	19.1	—	69.1[d]	2.38	2.00	28	199	0.067	2,970
3	Scholz	47.5	47.5	5.0	73.0	59.3	2.69	5.75	14	19	0.025	760
4	Scholz	42.5	42.5	15.0	74.4	60.6	2.69	5.63	14	56	0.024	2,335
5	Scholz	23.8	71.2	5.0	66.3	63.1	2.65	5.75	14	27	0.042	640
6	Scholz	21.2	63.8	15.0	69.7	66.8	2.69	5.75	14	39	0.017	2,295
7	Scholz	0.0	100.0	0.0	73.7	67.6	2.69	5.25	14	15	0.019	790
8	PP-620 (gypsum)	0.0	100.0	0.0	75.6	77.3	2.69	5.63	14	10	0.045	220
9	Scholz	40.0	40.0	20.0[e]	72.0	61.5	2.69	5.25	14	97	0.014	6,930
10	Scholz	40.0	40.0	20.0[e]	72.0	62.6	2.69	5.38	28	223	0.021	10,340
11	Scholz	40.0	40.0	20.0[e]	61.1	58.3[f]	2.69	5.31	28	165	0.022	7,420
12	PP-620 (gypsum)	40.0	40.0	20.0[e]	70.0	68.0	2.69	5.50	28	244	0.009	28,400

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[a] Samples 1 and 2 were mixed with an excess of water, poured into a mold, allowed to settle, and left to cure under water for four weeks.

[b] FGD product solids, ash-free, dried.

[c] Contains 19.1% portland cement.

[d] After curing.

[e] Contains 20% portland cement, equivalent to 12-13% CaO.

[f] Mixture was plastic and could not be compacted; it was rodded to eliminate air.

is the deformation at failure. The modulus of the elasticity is the stress divided by the strain at failure. The modulus is an indication of the sample's resistance to deformation; i.e., it is the stress necessary to produce a unit strain.

Included for comparison in Table VIII-8 are the measured unconfined compressive strengths for untreated, compacted samples of dual alkali sulfite and gypsum. These can be considered base cases to which the characteristics of the various treated samples can be compared. Samples 1 and 2, which were cured under water for 28 days, exhibited compressive strengths of 80 psi and about 300 psi, respectively. While those strengths clearly indicated that treatment had had an effect, the fact that the test specimens were only about two inches high could have resulted in erroneously high apparent unconfined compressive strengths. The remaining samples had height:diameter ratios of about 2:1, which was more appropriate for unconfined compression testing.

Samples 3-6 which contained varying proportions of fly ash and quicklime, and which were not cured under water, showed small increases in unconfined compressive strength over the untreated materials. Samples 4 and 6, which contained the larger amount of quicklime, had the higher strengths. At a constant 15% CaO, doubling the amount of fly ash also resulted in a higher strength.

Samples 9-12 contained 20 wt % portland cement as a calcium source instead of quicklime. By comparing samples 9 and 10, the increase in strength with additional curing time can be seen clearly. During the second fourteen days of curing, the compressive strengths more than doubled. Sample 11 had the same dry composition as sample 10, but it was prepared in the presence of more moisture, so that it could not be compacted because of its plasticity. Consequently, the mixture could only be rodded in the mold. After two days of curing it had become sufficiently rigid so that it could be removed from the mold and allowed to cure at 100% relative humidity with the other samples. However, its strength after twenty-eight days was somewhat lower than sample 10 which had been compacted. A sample of dual alkali gypsum was treated in a manner identical to that of sample 10; after twenty-eight days of curing it exhibited a somewhat greater unconfined compressive strength than did the dual alkali sulfite.

In summary, the chemical treatment procedures tested produced small, but significant, increases in the unconfined compressive strengths of the dual alkali solids. As a point of comparison, concrete generally has unconfined compressive strengths in excess of 2,000 psi and moduli of elasticity greater than 2,000,000. Thus, the treated solids, while considerably stronger than untreated materials, did not have the concrete-like characteristics required for materials of construction.

An attempt was made to measure the permeability of one sample of treated dual alkali sulfite (identical to sample 10 in Table VIII-8). For some reason, an apparent permeability of 2×10^{-4} cm/sec (not substantially different from untreated material) was measured in that test. It could not be determined whether the treated material was, in fact, that permeable, or whether the high value was due to experimental error. However, permeabilities of 5.5 x 10^{-6} and 5.6 x 10^{-6} cm/sec have been reported for treated dual alkali sulfite after eight days and twenty-nine days of curing, respectively, in the parallel study conducted for Southern Company Services[2].

Another treated sample, identical to the one whose permeability was measured, was subjected to the accelerated leaching test described in Section G. As shown in Table VIII-9, the concentration of both sodium and calcium in the two fractions of leachate collected from the treated material was considerably lower than for the untreated dual alkali sulfite. The reductions in the concentrations of sodium by factors of three and two, respectively, in the first and second leachate fractions could have been the result of the dilution of the calcium sulfite solids by the addition of fly ash and portland cement. However, the cementation reaction seemed to reduce the concentration of dissolved calcium quite markedly. If both the sodium and calcium are considered to be present as sulfates, the concentration of TDS in the first fraction of leachate collected from the treated material corresponds to about 3,500 ppm, a significant reduction from the 11,000 ppm of TDS in the first fraction collected from the untreated material.

In the parallel effort mentioned previously[2], samples of dual alkali sulfite were treated, cured, and tested for leachability by shaking samples of the solids, either treated or untreated, with four times their weight of water for 48 hours. Treatment reduced the concentrations of TDS in the wash liquors by factors ranging from 2 to nearly 5.

I. CONCLUSIONS

Limited testing was performed to characterize the basic physical and chemical properties of ash-free waste filter cakes produced in the two most successful dual alkali modes piloted -- concentrated and dilute active sodium modes with lime regeneration. Testing included: analysis of major chemical constituents; crystalline morphology via X-ray diffraction and scanning electron microscopy; unconfined compressive strength; compaction moisture/density relationship; permeability; leaching behavior; and the effects of treatment with lime (or portland cement) and fly ash on the physical properties.

The concentrated mode filter cake that was tested was produced in the prototype system using the two-stage reactor. The cake was a mixture of calcium sulfite and sulfate (about 15% calcium sulfate) and contained 55% solids. The crystalline structure of the solids was rosette-like agglomerates of needles characteristic of the concentrated mode operation. X-ray diffraction data and chemical analyses indicate that the calcium sulfite and calcium sulfate were coprecipitated as a mixed crystal of hemihydrate salts. There was no evidence of any appreciable amount of gypsum ($CaSO_4 \cdot 2H_2O$) in the solids.

TABLE VIII-9

EFFECT OF TREATMENT ON LEACHING OF SODIUM AND CALCIUM FROM DUAL ALKALI SULFITE

Sample	Eluate Fraction	Volume of Fraction (ml)	Cum. Void Volume	$[Na^+]$ ppm	$[Ca^{++}]$ ppm
Treated Dual Alkali Sulfite[a]	1	339	1.33	3,120	39
	2	338	2.66	300	180
Untreated Dual Alkali Sulfite	1	396	1.56	3,100	520
	2	312	2.78	600	598

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[a] Treated identically to sample 10, Table VIII-4.

The dilute mode filter cake was essentially pure gypsum produced in the pilot plant under conditions of intentional oxidation. The solids crystals were monoclinic and the filter cake contained approximately 80% insoluble solids.

The mixed sulfite/sulfate solids had the appearance and physical properties similar to a silt-like soil and handled much like a moist powder. The gypsum, on the other hand, was much more grainy and had the consistency of a sandy soil. The unconfined compressive strengths of both materials were in the range of typical soils, 10-15 psi, and both had optimum dry densities in the range of 75% solids. The coefficient of the permeability of the compacted sulfite/sulfate solids ranged from about 3×10^{-4} to 5×10^{-5} cm/second. The permeability of dual alkali gypsum was 2×10^{-5} cm/sec. These values are within the range of published data on the coefficients of permeability of gypsum and sulfite-rich solids produced in FGD systems.[1]

The treatment of the sulfite/sulfate filter cake was studied using various mixtures of lime (or portland cement), filter cake, and fly ash. This work showed that the concentrated mode solids could be treated in a fashion similar to the treatment of solids from direct lime and limestone scrubbing systems with similar effects on the mechanical properties. Testing performed on prototype system concentrated dual alkali solids by IU Conversion Systems (IUCS) indicates that the coefficient of permeability of treated filter cake was about 5×10^{-6} cm/sec using standard treatment mixes.

Accelerated leaching tests and elutriate analyses performed on untreated samples both at ADL and IUCS showed that the initial and "steady-state" concentrations of soluble species that can be leached, notably total dissolved solids (TDS) and total oxidizable sulfur (TOS), will be very dependent upon the initial conditions and composition of the solids as affected by the degree of cake washing, ratio of sulfate-to-sulfite, chloride concentration in the gas, etc. and the manner of solids handling and disposal. TDS levels in the initial leachate can range from a few thousand ppm to about ten thousand ppm, and "steady-state" concentrations (after the first few pore volume displacements) can vary from a few hundred ppm to approximately two thousand ppm. Similarly, TOS levels can range from essentially nil to up to fifty ppm. These concentrations are consistent with the range of published data for leachates from solids generated in direct lime and limestone scrubbing systems.

Testing performed by IUCS on the treatment of the filter cake indicated significant reductions in both initial and "steady-state" levels of TDS in leachates. Depending upon the type of treatment, reductions of 50% to 80% were observed.

In all physical properties testing performed at ADL, samples were prepared in accordance with standard soil-mechanics testing procedures. These procedures required, as a part of the sample preparation, the drying and rewetting of the filter cake to achieve a desired solids content. While the samples were dried at a temperature of 83°C to prevent loss of water of hydration, there is still concern that the drying/rewetting procedure resulted in some changes in the behavior of the material, particularly in the case of the rosette-like crystals produced in the concentrated mode operation. However, the results of these limited tests are believed to be indicative of the general behavior of the dual alkali solids. More exhaustive testing on both as-received samples and samples prepared in accordance with standard soil testing procedures is required to assess the effects of sample preparation on test results.

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Proceedings of the Sixth Flue Gas Desulfurization Symposium, Environmental Protection Agency, New Orleans, Louisiana, March 8-11, 1976, pp. 53-78

In Japan, twenty-four double alkali type flue gas desulfurization process plants have been put in operation since the beginning of 1973. The largest number of plant sites have been developed by Showa Denko. These systems are designed to use Na_2SO_3 as the absorbent and $CaCO_3$ as the precipitant. Another large-scale developer, a combine of Kureha Chemical Industry and Kawasaki Heavy Industries, have completed plants at four electric power plant sites.

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Proceedings of the Fifth Flue Gas Desulfurization Symposium, Environmental Protection Agency, Atlanta, Georgia, November 1974, pp. 1127-49

A description of the pilot plant operations conducted in a joint program between Monsanto Enviro-Chem. Systems, Inc. and Indianapolis Power and Light Company. Ethanolamine is used as the alkaline agent for absorption in this dual alkali type process, since it can be readily regenerated with lime.

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Proceedings of the Sixth Flue Gas Desulfurization Symposium, Environmental Protection Agency, New Orleans, Louisiana, March 8-11, 1976, pp. 545-62

The process designed by Envirotech Corporation is available in two modes. The dilute mode for use with low sulfur coals utilizes NaOH in the scrubber, $Ca(OH)_2$ to regenerate the scrubber liquor, and a softening agent to reduce the calcium ion level in the liquor before it is returned to the scrubber. In the concentrated mode sodium sulfite/bisulfite is used to remove SO_x. Design modifications for use with high chloride coal are presented.

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INHIBITION OF THE OXIDATION OF SULFITES IN AQUEOUS SOLUTION BY AIR
Czech Patent 145, 743, October 15, 1972, 3p.

A method for inhibiting the oxidation of sulfite ions to sulfate ions through the use of a solution of formaldehyde which forms an aldehyde-bisulfite complex thereby blocking the formation of oxygen radicals.

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SULFUR DIOXIDE REMOVAL USING SOLUBLE SULFITES
Presented at Rocky Mountain States Section, Air Pollution Control Assoc.,
Colorado Springs, Colorado, April 30, 1974, 34p.

A comparison of the process chemistry of double-alkali systems. The author describes the method which uses NaOH as the absorption solution as dilute double-alkali and the FMC Corp. system in which the absorbing solution is sodium sulfite as concentrated double alkali since the sulfite and bisulfite concentration typically totals above 1.0 molar. Capital and operating cost data are reported for these two systems.

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ADSORPTION, ORIENTED OVERGROWTH AND MIXED-CRYSTAL FORMATION
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Research on mixed-crystal formation shows that where a secondary substance -- an impurity -- precipitates on a certain plane or planes of the primary crystal there is modification of the crystal habit.

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SOME ASPECTS OF THE HOMOGENEOUS KINETICS OF SULFITE OXIDATION
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A study of the homogeneous kinetics and catalysis of sodium sulfite using a rapid-mixing method. This technique allowed the reaction of already dissolved oxygen, thus eliminating possible errors due to the interphase transfer of oxygen. The experimental findings showed that: (1) the reaction rate was independent of oxygen concentration; (2) the reaction order was 1.5 with respect to sulfite concentration; and (3) the reaction rate was proportional to the square root of the total concentration of cobalt added to the reacting solution.

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SULFUR DEVELOPMENTS: SULFUR DIOXIDE REMOVAL IN A DOUBLE-ALKALI PLANT
Chem. Eng. Prog., 69 (12): 47-53, 1973

Pilot plant operations of a double alkali system are described. The calcium sulfate waste is disposed of by means of landfill. The system was designed by Envirotech Corp. and the facility is located at a Salt Lake City power station.

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Preprint of paper presented at the 164th National American Chemical Society Meeting, New York City, August 28-September 1, 1972, pp. 43-9

Results of laboratory studies on the use of antioxidants to inhibit the formation of sulfates in alkaline solutions of sulfite and bisulfite ions. The inhibitors listed are benzyl alcohol, phenol, and hydroquinone.

Dahlstrom, D.A. and Cornell, C.F.
SULFUR DIOXIDE SCRUBBING PROCESS
U.S. Patent 3,873,532, March 25, 1975, assigned to Envirotech Corporation, Menlo Park, California

This process utilizes a sodium-based aqueous scrubbing solution to absorb stack gases, followed by a regeneration of the solution with slaked lime. This solution is then reacted with sodium carbonate, to reduce calcium ion concentration and solids content, before it is returned to the absorption apparatus.

Devitt, T.W.; Isaacs, G.A.; and Laseke, B.A.
STATUS OF FLUE GAS DESULFURIZATION SYSTEMS IN THE UNITED STATES
Proceedings of the Sixth Flue Gas Desulfurization Symposium, Environmental Protection Agency, New Orleans, Louisiana, March 8, 1976, pp. 13-51

A discussion of numbers and types of FGD systems, operational, under construction, or planned. Reports on a number of individual facilities presents values for process designs and operating parameters. Study is on-going and further reports will be generated, including data on dual alkali systems.

De Waal, K.J.A. and Okeson, J.C.
THE OXIDATION OF AQUEOUS SODIUM SULPHITE SOLUTIONS
Chemical Engineering Science, 21: 559-72, 1966

A method is suggested for the determination of the interfacial area between a gas and a liquid and of the surface renewal rate of this interface. This method is based upon the oxidation of a concentrated aqueous sulphite solution with gaseous oxygen in the presence of cobaltous sulphate as a catalyst.

Dingo, T.T.
PERFORMANCE CHARACTERISTICS OF AN INDUSTRIAL SIZE DUAL ALKALI SO_2 REMOVAL SYSTEM
Proceedings of the Fifth Flue Gas Desulfurization Symposium, Environmental Protection Agency, Atlanta, Georgia, November 1974, pp. 517-37

A review of the process chemistry, equipment and performance characteristics of the General Motors double alkali SO_2 Control System.

Draemel, D.C.
REGENERATION CHEMISTRY OF SODIUM-BASED DOUBLE-ALKALI SCRUBBING PROCESS
EPA-R2-73-186, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1973, 37 pp.

A report of the results of a study of the reactions of calcium hydroxide and calcium carbonate with the aqueous (sodium, sulfite, bisulfite, and sulfate) system. The objectives were to study various reactions of importance in the sodium-based double alkali process and to define possible operating modes for the process.

Draemel, D.C.
AN EPA OVERVIEW OF SODIUM-BASED DOUBLE ALKALI PROCESSES
PART I. A VIEW OF THE PROCESS CHEMISTRY OF IDENTIFIABLE AND ATTRACTIVE SCHEMES
Proceedings of the Fourth Flue Gas Desulfurization Symposium, Environmental Protection Agency, New Orleans, Louisiana, 1973, pp. 997-1018

The process chemistry of double alkali scrubbing is presented, and five double alkali operating schemes are outlined. Sulfur oxides are absorbed into a sulfite/bisulfite buffer solution, shifting the pH down and increasing the bisulfite concentration. The liquor from the scrubber may then be treated with limestone to precipitate calcium sulfite and neutralize the bisulfite, and the liquor from the scrubber or the limestone reaction vessel may be treated with lime to precipitate calcium sulfite and possible calcium sulfate. The oxidation of absorbed sulfur requires the regeneration of sulfate. Calcium ion concentrations in the scrubber can be controlled by softening steps in the liquor loop.

Drehmel, D.C.
WET LIMESTONE SCRUBBING OF SULFUR OXIDES: LIMESTONE SELECTION
Proceedings of the Second International Lime/Limestone Wet Scrubbing Symposium, New Orleans, Louisiana, November 8-12, 1971

A report of tests made on different types of limestone to determine their dissolution rates in acid media and their sulfur oxide removal efficiencies in a batch scrubber.

Elder, H.W.; Princiotta, F.T.; Hollinden, G.A.; Gage, S.J.
SULFUR OXIDE CONTROL TECHNOLOGY
VISITS IN JAPAN - AUGUST 1972
U.S. Government Interagency Report, Muscle Shoals, Alabama, October 30, 1972, 113 pp.

During the period August 2 to August 16, 1972, a U.S. Government team visited organizations in Japan to evaluate technology for control of sulfur dioxide emissions. The Tennessee Valley Authority, the EPA and the Office of Science and Technology (Executive Office of the President) were represented. They visited 14 companies and the Japan Environmental Agency. The primary purpose of the trip was to observe full-scale scrubbing systems in operation on coal fired power plants. Systems discussed include dual alkali.

Ellison, W.; Heden, S.D.; and Kominek, E.G.
SYSTEM RELIABILITY AND ENVIRONMENTAL IMPACT OF SO_2 SCRUBBING PROCESSES
Proceedings of The Coal Utilization Symposium-Focus SO_2 Emission Control, National Coal Association, Louisville, Kentucky, 1974, p.130-52

A discussion of the major problems of system design and operation related to scrubbing processes. It includes information on (1) the chemistry of throw-away systems e.g. lime/limestone and double alkali, (2) reliability design with regard to major equipment for these processes and (3) system development for the double-alkali technique of scrubbing.

Epstein, M.
EPA ALKALI SCRUBBING TEST FACILITY: SUMMARY OF TESTING THROUGH OCTOBER 1974
EPA-650/2-75-047, Bechtel Inc., San Francisco, California, June 1975, 506 p.

This report on the EPA test facility at Shawnee Power Station includes data on sodium carbonate (soda ash) scrubbing. Models are presented for predicting SO_2 removal in sodium carbonate.

Epstein, M.; Sybert, L.; Wang, S.C.; Leivo, C.C.; Abdul-Sattar, A.H.; Princiotta, F.T.; Williams, J.E.; Borgwardt, R.H.; Statnick, R.M.; and Drehmel, D.C.
PRELIMINARY REPORT OF TEST RESULTS FROM THE EPA ALKALI SCRUBBING TEST FACILITIES AT THE TVA SHAWNEE POWER PLANT AND AT RESEARCH TRIANGLE PARK
Presented at an Environmental Protection Agency Public Briefing at Research Triangle Park, N.C., December 19, 1973

In June, 1968 EPA initiated a program to test a prototype lime and limestone wet-scrubbing system for removing SO_2 and particulates from flue gases.

This report presents the results, through early December, 1973, of (1) limestone and lime reliability verification and long-term reliability testing at the Shawnee Prototype Facility and (2) limestone and lime testing at the EPA Pilot Facility at Research Triangle Park, N.C.

Field, E.L.; LaMantia, C.R.; Lunt, R.R.; Oberholtzer, J.E.; and Valentine, J.R.
MULTISTAGE PROCESS FOR REMOVING SULFUR DIOXIDE FROM STACK GASES
U.S. Patent 3,994,669, March 16, 1976, assigned to Combustion Equipment Associates, Inc., New York, NY

A method and apparatus for removing sulfur dioxide from stack gases by means of an alkali scrubbing solution which is regenerated by treatment with calcium compounds in at least two separate reaction stages to produce calcium sulfate and calcium sulfite prior to recycling the scrubber solution.

Fitch, B.
BATCH TESTS PREDICT THICKENER PERFORMANCE
Chemical Engineering, August 23, 1971, pp. 83-88

Discussion of the advantages and limitations of several methods for using batch settling data to design thickeners. The paper includes a review of the fundamental equation of solids flux derived by Coe and Clevenger, as well as several thickening models and design criteria.

Frazier, J.F.
REMOVAL OF SULFUR OXIDES FROM INDUSTRIAL BOILER FLUE GASES
National Eng., 75 (8): 6-9, 1971

A discussion of costs of the chemical requirements and cost of equipment for the dual-alkali method for desulfurizing flue gases. Also has a table of factors for estimating quantities of chemicals used in the process.

Galeano, S.F. and Harding, C.I.
SULFUR DIOXIDE REMOVAL AND RECOVERY FROM PULP MILL POWER PLANTS
J. Air Pollut. Control Assoc., 17 (8): 536-9, August 1967

The use of soda ash liquor to scrub SO_2-rich power plant flue gases was studied using an Airetron pilot scrubber with a maximum capacity of 3000 cfm. The relative effects of the major operating variables -- temperature, soda ash concentration, and the gas/liquid flow ratio -- on the absorption phenomenon were determined.

Harris, I.F. and Roper, G.H.
THE ABSORPTION OF OXYGEN BY SODIUM SULPHITE ON A SIEVE PLATE
Can. J. Chem. Eng., 42: 34-7, February 1964

The oxidation of sodium sulfite on a single sieve plate indicates that the reaction rate constant is substantially greater than that reported in the literature.

Horlacher, W.R.; Barnard, R.E.; Teague, R.K. and Hayden, P.L.
FOUR SULFUR DIOXIDE REMOVAL SYSTEMS
Chem. Eng. Progr., 68 (8): 43-50, 1972

A description of equipment and methods of operation developed by Monsanto Enviro-Chem Systems, which includes double alkali type process.

Howard, H. and Stantial, F.G.
METHOD OF RECOVERING SULFUR DIOXIDE FURNACE GASES
U.S. Patent #1,271,899, July 9, 1918, 2p.

Initial patent on the method of scrubbing flue gases with a sodium salt solution followed by reaction of the scrubber effluent with calcium hydroxide to precipitate calcium sulfite and regenerate the scrubber feed.

Hurwitz, E.; Ciabettari, E.; Wolff, R.A.; and Bernstein, I.
POLLUTION CONTROL BY AIR OXIDATION OF WASTE SULFITE LIQUORS
Industrial and Eng. Chem., 51 (10): 1301-4, October 1959

Semi-pilot plant investigation of the oxidation of sulfite wastes with tests of catalysts and their effect on the oxidizing rate. The equipment used in the experiment is described.

Johnstone, H.F.; Read, H.J.; and Blankmeyer, H.C.
RECOVERY OF SULFUR DIOXIDE FROM WASTE GASES: EQUILIBRIUM VAPOR PRESSURES OVER SULFITE-BISULFITE SOLUTIONS
Industrial and Eng. Chem., 30 (1): 101-9, 1938

Partial vapor pressures were measured over a temperature range from 35° - 90°C for an extensive series of concentrations and compositions of sulfite-bisulfite solutions of sodium and methylamine. Sufficient data for a number of other sulfite-bisulfite solutions are reported to show the effect of the nature of the solution on the temperature coefficient of the vapor pressure of sulfur dioxide.

Kaplan, N.
INTRODUCTION TO DOUBLE ALKALI FLUE GAS DESULFURIZATION TECHNOLOGY
Proceedings of the Sixth Flue Gas Desulfurization Symposium, Environmental Protection Agency, New Orleans, Louisiana, March 8-11, 1976, pp. 387-422

A detailed description of the sodium/calcium based double alkali processes to date. Special terminology which has evolved with the technology is defined and discussed. These include such terms as absorption/regeneration chemistry, active alkali, active sodium and TOS (total oxidizable sulfur). Significant process and design factors with some cost information are carefully reviewed. EPA's Research and Development program on double alkali technology is outlined.

Kaplan, N.
AN OVERVIEW OF DOUBLE ALKALI PROCESSES FOR FLUE GAS DESULFURIZATION
Proceedings of the Fifth Flue Gas Desulfurization Symposium, Environmental Protection Agency, Atlanta, Georgia, November 1974, pp. 387-422

The chemistry and process design considerations applicable to sodium/calcium double alkali systems are presented. Technical terminology associated with these systems is defined.

The developmental efforts and full scale applications of the technology by Envirotech, FMC, General Motors, Zurn Industries, Arthur D. Little/Combustion Equipment Associates, Kawasaki Heavy Industries/Kureha Chemical Industry and Showa Denko KK are discussed with reference to appropriate flowsheets. Planned applications of technology by these companies are also discussed and tabulated.

Kaplan, N.
AN EPA OVERVIEW OF SODIUM BASED DOUBLE ALKALI PROCESSES. PART II - STATUS OF TECHNOLOGY AND DESCRIPTION OF ATTRACTIVE SCHEMES
Proceedings of the Fourth Flue Gas Desulfurization Symposium, Enviromental Protection Agency, New Orleans, Louisiana, 1973, pp. 1019-60

Criteria for evaluating double alkali schemes are described and include sulfate removal, scale prevention, water balance, waste product washing, SO_2 removal and capital and operating costs. Flowsheets for potentially attractive schemes of operation are presented and compared. Status of the technology is reviewed. The EPA/A.D. Little double alkali development program plan and general philosophy are described.

Kawamoto, K.; Tsuno, T. and Namiki, Y. (Mitsubishi Chemical Industries Co., Ltd.)
ANTIOXIDANTS FOR SULFITE SOLUTIONS
German Patent #2,243,201, March 15, 1973, 16p.

A patent covering the use of the following classes of antioxidants and their effects on solutions of sodium bisulfite, sodium sulfite, potassium bisulfite and potassium sulfite. (1) substituted phenols, (2) tris (alkyphenyl) phosphates, (3) trialkyl phosphites and (4) alpha glycerol esters. Methods for their use are also in this patent.

Kerr, [illegible].P.
AQUEOUS SODIUM SULFITE, BISULFITE AND SULFATE EQUILIBRIA
AIChE, J., 20 (6): 1213-5, November 1974

A description and formulas for use in calculating parameters for scrubber design. The subject areas explored are the equilibrium SO_2 partial pressure over the solution and liquid composition with the following specifications: temperature, total pressure, sodium ion concentration, total dissolved sulfur concentration, SO_2 partial pressure, and sulfate ion concentration.

LaMantia, C.R.; Bangel, E.R.; Phillips, R.; and Lamb, T.J.
EMISSION CONTROL FOR SMALL SCALE FACILITIES
A Chemical Engineering Progress Technical Manual, Amer. Institute of
Chem. Engineers, New York, NY, 1971, pp. 142-50

A study to evaluate the various approaches for control of SO_2 according to the following criteria: emission reduction, technical risk, reliability, appropriateness of the process and capital investment and operating costs. Dual alkali process is among those considered.

LaMantia, C.R.; Lamb, T.J.; Sommer, R.S.; Shah, I.S.; and Falco, J.M.
SULFUR DIOXIDE EMISSION CONTROL FOR INDUSTRIAL BOILERS
Paper presented at Industrial Coal Conference, Purdue University,
October 5, 1972, 18 pp.

A discussion of the overall problem of SO_2 control for industrial scale boilers and description of three appropriate scrubbing processes (1) once-through sodium, (2) direct lime/limestone and (3) sodium with lime regeneration (includes cost data).

LaMantia, C.R.; Field, E.L.; Lamb, T.J.; Oberholtzer, J.E.; Valentine, J.R.
SULFUR DIOXIDE CONTROL PROCESS STUDY - SODIUM SCRUBBING WITH LIME
REGENERATION
A Report to the State of Illinois, Institute of Environmental Quality,
Arthur D. Little, Inc., Cambridge, Massachusetts, January 1972, 64 p.

An experimental laboratory investigation of the regeneration step of the sodium scrubbing process with lime regeneration. It includes an analysis of the experimental results, a conceptual process design, and a preliminary estimate of capital and operating costs for a representative size, full-scale, industrial boiler installation.

LaMantia, C.R. and Raben, I.A.
SOME ALTERNATES FOR SO_2 CONTROL
Proceedings of the Coal Utilization Symposium, Louisville, Kentucky, October 22-4, 1974, pp. 153-61

Technology of three systems of gas scrubbing -- sodium, alkali fly ash, and dual alkali being used on an industrial scale are described. The technology is the result of cooperative efforts between Arthur D. Little, Inc. and Combustion Equipment Associates, Inc.

LaMantia, C.R.; Lunt, R.R.; Oberholtzer, J.E.; Field, E.L.; and Kaplan, N.
EPA-ADL DUAL ALKALI PROGRAM -- INTERIM RESULTS
Proceedings of the Fifth Flue Gas Desulfurization Symposium, Environmental Protection Agency, Atlanta, Georgia, November 1974, pp. 549-665

A report of the laboratory and pilot plant results obtained on lime and limestone regeneration of concentrated and dilute sodium scrubbing solutions as well as work performed on the sulfuric acid treatment scheme for soluble sulfate precipitation.

LaMantia, C.R.; Lunt, R.R.; and Shah, I.S.
DUAL ALKALI PROCESS FOR SO_2 CONTROL
Proceedings of the Sixty-sixth American Institute of Chemical Engineers Symposium on Air: II. Control of NO_x and SO_x Emissions, Philadelphia, Pennsylvania, 1975, Series #148, 71, 324-9

Laboratory development work is discussed including batch reactor experiments and continuous reactor experiments. Pilot plant facility is described and performance data on the scrubber system and regeneration reactor system are presented.

LaMantia, C.R.; Lunt, R.R.; Rush, R.E.; Frank, T.M.; and Kaplan, N.
OPERATING EXPERIENCE--CEA/ADL DUAL ALKALI PROTOTYPE SYSTEM AT GULF POWER/SOUTHERN SERVICES, INC.
Proceedings of the Sixth Flue Gas Desulfurization Symposium, Environmental Protection Agency, New Orleans, Louisiana, March 8-11, 1976, pp. 423-69

A description of the 20-megawatt dual alkali SO_2 control facility at Gulf Power Company's Scholz Steam Plant. The system was developed, designed and installed by Combustion Equipment Associates, Inc. and Arthur D. Little, Inc. for Gulf Power/Southern Services, Inc. and tested as part of EPA's Industrial Environmental Research Laboratory program. Operating history and system performance are reviewed from initial start-up through the first year of operation.

Larson, J.W.
THERMODYNAMICS OF DIVALENT METAL SULFATE DISSOCIATION AND THE STRUCTURES OF THE SOLVATED METAL SULFATE ION PAIR
J. of Phys. Chem., 74 (18): 3392-6, September 3, 1970

Data for the heats and entropies of dissociation of divalent metal sulfate ion pairs are reported. These calculations made use of the very precise heats of dilution measured by Lange or his coworkers.

Legatski, L.K.; Johnson, K.E. and Lee, L.Y.
THE FMC CONCENTRATED DOUBLE-ALKALI PROCESS
Proceedings of the Sixth Flue Gas Desulfurization Symposium, Environmental Protection Agency, New Orleans, Louisiana, March 8-11, 1976, pp. 471-502

This process utilizes Na_2SO_3 in the scrubber. In the regeneration step, which is pH controlled, $Ca(OH)_2$ is employed. Development efforts such as scrubber performance, sulfate formation rate studies, and lime reactor performance show strategy employed. Plant demonstration descriptions include some capital and operating cost data.

Leo, P.P. and Rossoff, J.
CONTROL OF WASTE AND WATER POLLUTION FROM POWER PLANT FLUE GAS CLEANING SYSTEMS: FIRST ANNUAL R AND D REPORT
EPA-600/7-76-018, October 1976

This report summarizes and assesses the state of research and development as of 1975 in the fields of nonregenerable flue gas cleaning waste treatment, utilization and disposal, as well as water reuse technology for coal-fired utility power plants.

Lewis, P.H.
OPERATING EXPERIENCE WITH THE ZURN DOUBLE ALKALI FLUE GAS DESULFURIZATION PROCESS
Proceedings of the Sixth Flue Gas Desulfurization Symposium, Environmental Protection Agency, New Orleans, Louisiana, March 8-11, 1976, pp. 503-14

This system in use at a plant of the Caterpillar Tractor Co. utilizes a dilute NaOH solution for gas scrubbing. The spent solution is regenerated with $Ca(OH)_2$, after which a "softening" agent Na_2CO_3 is added to further precipitate calcium before the sodium hydroxide solution is returned to the scrubber.

Linek, V.
THE OXIDATION OF AQUEOUS SULPHITE SOLUTIONS
Chem. Eng. Science, 26: 491-6, 1971

A discussion of data in the literature concerned with the absorption rate of oxygen in aqueous sulfite solutions and the effects of impurities, pH, and inert gas on the absorption rate.

Linek, V. and Tvrdik, J.
GENERALIZATION OF KINETIC DATA ON SULPHITE OXIDATION SYSTEMS
Biotechnol. and Bioeng., 13 (3): 353-69, May 1971

A study of mass transfer in gas-liquid systems utilizing the oxidation of aqueous sulfate solutions in the presence of a cobaltous sulfate catalyst. The derived data was used as a basis for a method of kinetic data processing.

Linek, V. and Mayrhoferova, J.
THE KINETICS OF OXIDATION OF AQUEOUS SODIUM SULPHITE SOLUTION
Chem. Eng. Science, 25: 787-800, 1970

The kinetic data of the reaction were calculated from the absorption rate of oxygen into the mechanically agitated sulphite solutions. It was found that the reaction order in oxygen depends on the oxygen concentration in the liquid phase at the interface. The reaction is first order for oxygen concentrations higher than approximately 6. 10^{-4} kmol.m^{-3} at the interface and second order for lower oxygen concentrations.

Lunt, R.R.; Rush, R.E.; Frank, T.E.; LaMantia, C.R.
STARTUP AND OPERATION OF THE CEA/ADL ALKALI PROCESS AT GULF POWER/ SOUTHERN SERVICES
Presented at the Sixty-eighth Annual Meeting of the American Institute of Chemical Engineers, Los Angeles, California, November 16-20, 1975, 36 p.

A description of the 20-megawatt, dual alkali SO_2 control process at Gulf Power Company's Scholz Steam Plant and summary of the results of the initial months of operation. The system was developed, designed and installed by Combustion Equipment Associates, Inc./Arthur D. Little, Inc. for Southern Services, Inc. at Gulf Power Company's Scholz Plant in Sneads, Florida, and started up in February 1975.

Marshall, W.L. and Jones, E.V.
SECOND DISSOCIATION CONSTANT OF SULFURIC ACID FROM 25-350° EVALUATED FROM SOLUBILITIES OF CALCIUM SULFATE IN SULFURIC ACID SOLUTIONS
J. Phys. Chem., 70 (12): 4028-40, 1966

A documentation of values from second dissociation quotients and constants for sulfuric acid determined from extensive solubility measurements of calcium sulfate and its hydrates in aqueous sulfuric acid at specific concentrations and temperatures.

Marshall, W.L. and Slusher, R.
DEBYE-HUECKEL CORRELATED SOLUBILITIES OF CALCIUM SULFATE IN WATER AND IN AQUEOUS SODIUM NITRATE AND LITHIUM NITRATE SOLUTIONS OF MOLALITY 0 TO 6 MOLE KG^{-1} AND AT TEMPERATURES FROM 398 TO 623°K
J. Chem. Thermodyn., 5 (2): 189-97, 1973

McGlamery, G.G.; Faucett, H.L.; Torstrick, R.L.; and Henson, L.J.
FLUE GAS DESULFURIZATION ECONOMICS
Proceedings of the Sixth Flue Gas Desulfurization Symposium, Environmental Protection Agency, New Orleans, Louisiana, March 8-11, 1976, pp. 79-99

Cost data for the double-alkali systems--Envirotech, CEA/ADL, and FMC are reported briefly. Study shows total investment and revenue requirements of the three systems are relatively close. More intensive evaluation of the most promising systems is planned.

Morita, T.
ANTIOXIDATION TREATMENT OF BISULFITES AND SULFITES
Japanese Patent 72, 20, 455, June 10, 1972, 3pp.

A patent covering the use of the following antioxidants as inhibitors in solutions of sulfites: p-aminophenol, p-aminophenol & sodium nitriloacetate, or the combination of p-aminophenol & sodium nitriloacetate & p-phenylenediamine.

Mo. , T.
POLLUTION CONTROL. 3. AIR POLLUTION CONTROL. WASTE GAS DESULFURIZATION BY THE SODIUM SULFITE-GYPSUM PROCESS
Kagaku, Kogyo, 23 (7): 915-21, 1972 (In Japanese)

Morita, T.
GAS DESULFURIZATION BY THE KUREHA SODIUM SULFITE-GYPSUM PROCESS
Sekko To Sekkai No. 151, 317-21, 1977 (Japan)

A review of a process for absorbing sulfur dioxide in a sodium sulfite solution and then treating the resulting solution with limestone to produce calcium sulfite and recover sodium sulfite -- the calcium sulfite is then oxidized to calcium sulfate.

Nilsson, G.; Rengemo, T.; and Sillen, L.
SOME SOLUTION EQUILIBRIA INVOLVING CALCIUM SULFITE AND CARBONATE
I. SIMPLE SOLUBILITY EQUILIBRIA OF CO_2, SO_2, $CaCO_3$ AND $CaSO_4$
Acta Chemica Scandinavica, 12 (5): 868-72, 1958

Onda, K.; Takeuchi, H. and Maeda, Y.
THE ABSORPTION OF OXYGEN INTO SODIUM SULPHITE SOLUTIONS IN A PACKED COLUMN
Chem. Eng. Science, 27: 449-51, 1972

A study of the absorption of oxygen into sodium sulphite solutions in the presence of cobalt sulphate as catalyst with the investigation directed to the influence of oxygen pressure on absorption rate and interfacial areas.

Onozuka, M.; Nomoto, K.I.; and Morita, T.
METHOD FOR PRODUCING CALCIUM SULFITE HEMIHYDRATE
U.S. Patent 3,848,070, November 12, 1974, assigned to Kureha Kagaku Kogyo Kabushiki Kaisha, Tokyo

A method comprising the use of an aqueous solution of sodium sulfite to absorb SO_2 from stack gases and subsequently reacting this solution with calcium carbonate under controlled conditions to form the product.

Edwards, R.
PERSONAL COMMUNICATION, I.U. CONVERSION SYSTEMS TO REED EDWARDS OF THE SOUTHERN COMPANY SERVICES
April, 1976

A report to Reed Edwards from IUCS, regarding limited chemical analyses and physical properties testing performed on waste solids generated by the prototype systems at the Scholz Steam Plant.

Phillips, R.J.
SULFUR DIOXIDE EMISSION CONTROL FOR INDUSTRIAL POWER PLANTS
Proceedings of the Second International Lime/Limestone Wet-Scrubbing Symposium, Environmental Protection Agency, New Orleans, Louisiana, May 14-17, 1973, 36p.

A description of the research and development done at General Motors on caustic wet scrubbing with lime regeneration from laboratory scale tests to pilot plant operations.

Piasecki, E.J.
EQUIPMENT PERFORMANCE WITH A COMMERCIAL DUAL-ALKALI SO_2 REMOVAL SYSTEM
Proceedings of the Fifth Flue Gas Desulfurization Symposium, Environmental Protection Agency, Atlanta, Georgia, 1974, pp. 539-48

A discussion of the GM dual alkali system and equipment design and performance.

Rand, M.C. and Gale, S.B.
KINETICS OF THE OXIDATION OF SULFITES BY DISSOLVED OXYGEN
Proceedings of the Fourth Conference on Principles Appl., Water Chem., Rudolphs Res. Rutgers State University, 1965, pp. 380-404

A review of the technical results in scientific publications in this subject area which appeared in the literature from 1897 to 1960.

Rawe, R.T.
SO_2 CONTROL FOR SMALL BOILERS
Pollut. Eng., 4 (1): 22-3, January/February 1972

An overview of caustic wet scrubbing for small scale industrial boilers with boiler steam capacities from about 50,000 to 500,000 lb/hr.

Reinders, W. and Vles, S.I.
REACTION VELOCITY OF OXYGEN WITH SOLUTIONS OF SOME INORGANIC SALTS
III. THE CATALYTIC OXIDATION OF SULPHITES
Rec. Trav. Chem., 44: 249-68, 1925

Details of a study on the oxidation of sulphite without and with a catalyst and with copper salts as catalysts. The reaction-velocity curve with respect to the pH was traced and the optimum velocity was found to lie at pH of 10. Two constituents ($SO_3^=$ and Cu^{++}) determine the velocity constants and both are strongly dependent on the pH. Lowering the pH decreases the velocity because the $SO_3^=$ ion concentration decreases with the formation HSO_3^- and H_2SO_3 so that at pH 3 scarcely and $SO_3^=$ ions exist and the velocity is very small.

Reith, T. and Beek, W.J.
THE OXIDATION OF AQUEOUS SODIUM SULPHITE SOLUTIONS
Chem. Eng. Science, 28: 1331-9, 1973

New experimental work on the kinetics of the absorption of oxygen in an aqueous solution of sodium sulphite with cobaltous sulphate as a catalyst. The data presented is compared with already published data.

Rengemo, T; Brune, U.; and Sillen, L.G.
SOME SOLUTION EQUILIBRIA INVOLVING CALCIUM SULFITE AND CARBONATE
II. THE EQUILIBRIUM BETWEEN CALCIUM SULFATE AND CALCIUM SULFITE IN AQUEOUS SOLUTIONS
Acta Chemica Scandinavica, 12: 873-7, 1958

Rochelle, G.T.
ECONOMICS OF FLUE GAS DESULFURIZATION
Proceedings of the Fourth Flue Gas Desulfurization Symposium, Environmental Protection Agency, New Orleans, Louisiana, 1977, pp. 103-32

A summary of results and conclusions of an analysis of the costs of flue gas desulfurization for fossil fuel boiler plants, includes data on dual alkali process costs.

Shah, I.S.
REMOVAL OF SULFUR DIOXIDE FROM GAS STREAMS
U.S. Patent 3,775,532, November 27, 1973, Assigned to Chemical Construction Corporation, New York, NY

A process for wet scrubbing of waste flue gas which employs an aqueous solution of sodium sulfite as the scrubber liquid, resulting in an aqueous sodium sulfite and sodium bisulfite mixture. Portions of this solution are treated in two separate procedures to precipitate calcium sulfite and calcium sulfate and thus prevent undesirable solids build-up in the circulating system.

Spalding, C.W. and Han, S.T.
ABSORPTION WITH CHEMICAL REACTION FROM A DILUTE GAS IN PACKED TOWERS
Tappi, 45 (3): 192-9, 1962

A review of the absorption in a liquid, of a dilute component of a gaseous mixture by chemical reaction on the basis of both the film and the penetration theories. The design procedure and operating characteristics of packed towers are discussed in the light of the theories and illustrated with SO_2-H_2O and SO_2-NaOH-H_2O systems.

Srivastava, R.D.; McMillan, A.F.; and Harris, I.J.
THE KINETICS OF OXIDATION OF SODIUM SULPHITE
Can. J. Chem. Eng., 46: 181-4, June 1968

A study of the kinetics of the reaction of sodium sulphite in aqueous solution without and with a catalyst of cobaltous sulphate. The reaction rate was found to be first order with respect to oxygen and variable order with respect to sulphite, and the accelerating effect of cobaltous catalyst was proportional to its concentration.

Wall, R.I.; Harris, H.C.; and Arnuad, J.L.
PROCESS FOR SEPARATING SULFUR OXIDES FROM GAS STREAMS
U.S. Patent 3,911,084, October 7, 1975, assigned to FMC Corporation, New York, NY

A scrubber solution of sodium sulfite-sodium bisulfite maintained at pH 6 is regenerated in a single stage step by addition of calcium hydroxide to precipitate calcium sulfite which is removed as waste. Solution is then returned to the scrubber liquor.

Wen, C.Y. and Uchida, S.
ABSORPTION OF SO_2 BY ALKALINE SOLUTIONS IN VENTURI SCRUBBER SYSTEMS
EPA-650/2-73-003, U.S. Environmental Protection Agency, West Virginia University, July 1973, 169pp.

A description of studies on SO_2 absorption from flue gases by water and alkaline solutions in venturi scrubbers, including recycle of the scrubbing liquor. Mathematical models are proposed for process momentum, heat and mass transfer in SO_2-$NaOH$-H_2O and SO_2-$CaCO_3$-H_2O systems. The momentum, heat and mass balances are used to describe the reactions taking place in the venturi scrubber.

Wesselingh, J.A. and Van't Hoog, A.C.
OXIDATION OF AQUEOUS SULPHITE SOLUTIONS: A MODEL REACTION FOR MEASUREMENTS IN GAS-LIQUID DISPERSIONS
Trans. Instn. Chem. Engrs., 48: T69-T74, 1970

A documentation of research methodology, oxygen pressure, specific absorption rate of oxygen versus pH, influence of impurities and also hydrodynamic conditions. Comparisons are made with existing kinetic data showing reasons for the discrepancies.

Whitney, R.P.; Han, S.T.; and Davis, J.L.
ON THE MECHANISM OF SULPHUR DIOXIDE ABSORPTION IN AQUEOUS MEDIA
Tappi, 36 (4): 172-5, 1953

A discussion of the absorption of sulphur dioxide in aqueous media -- water, sodium carbonate solution, and sodium sulphite solution.

Yagi, S. and Inoue, H.
THE ABSORPTION OF OXYGEN INTO SODIUM SULPHITE SOLUTION
Chem. Eng. Science, 17: 411-21, 1962

An investigation of the kinetics of absorption and the mechanism of absorption of oxygen in a sulphite solution.

Yeatts, L.B. and Marshall, W.L.
APPARENT INVARIANCE OF ACTIVITY COEFFICIENTS OF CALCIUM SULFATE AT CONSTANT IONIC STRENGTH AND TEMPERATURE IN THE SYSTEM $CaSO_4$-$NaSO_4$-$NaNO_3$-H_2O TO THE CRITICAL TEMPERATURE OF WATER. ASSOCIATION EQUILIBRIA
J. Phys. Chem., 73 (1): 81-90, 1969

XI. GLOSSARY

Active Sodium - Sodium associated with anions involved in SO_2 absorption reactions and includes sulfite, bisulfite, hydroxide and carbonate/bicarbonate. Total active sodium concentration is calculated as follows:

$$[Na^+]_{active} = 2 \times ([Na_2SO_3] + [Na_2CO_3]) + [NaHSO_3] + [NaOH] + [NaHCO_3]$$

Active Sodium Capacity - The equivalent amount of SO_2 which can be theoretically absorbed by the active sodium, with conversion to $NaHSO_3$. Active sodium capacity is defined by:

$$[Na^+]_{active} \text{ capacity} = [Na_2SO_3] + 2 \times [Na_2CO_3] + [NaOH] + [NaHCO_3]$$

Calcium Utilization - The percentage of the calcium in the lime or limestone which is present in the solid product as a calcium-sulfur salt. Calcium utilization is defined as:

$$\text{Calcium Utilization} = \frac{\text{mols } (CaSO_3 + CaSO_4) \text{ generated}}{\text{mol Ca fed}} \times 100\%$$

Concentrated Dual Alkali Modes - Modes of operation of the dual alkali process in which regeneration reactions produce solids containing $CaSO_3 \cdot \frac{1}{2}H_2O$ or a mixed crystal containing calcium sulfite and calcium sulfate hemihydrates, but not containing gypsum. Active sodium concentrations are usually higher than 0.15M Na^+ in concentrated mode solutions.

CSTR--Continuous Stirred Tank Reactor - A well-agitated, baffled reactor vessel having a uniform concentration of species throughout. At any time the concentrations in the effluent from a CSTR are equivalent to those within the vessel.

Dilute Dual Alkali Modes - Modes of operation of the dual alkali process in which regeneration reactions produce solids containing gypsum ($CaSO_4 \cdot 2H_2O$). Active sodium concentrations are usually lower than 0.15M Na^+ in dilute mode solutions.

Sulfate Formation - The oxidation of sulfite. The level of sulfate formation relative to SO_2 absorption is given by:

$$\text{Sulfate Formation} = \frac{\text{mols } SO_3^{=} \text{ oxidized}}{\text{mol } SO_2 \text{ removed}} \times 100\%$$

Sulfate Precipitation - The formation of $CaSO_4 \cdot XH_2O$ in soluble solids. The level of sulfate precipitation in the overall scheme is given by the ratio of calcium sulfate to the total calcium-sulfur salts produced:

$$\text{Sulfate Precipitation} = \frac{\text{mols } CaSO_4}{\text{mol } CaSO_X}$$

TDS--Total Dissolved Solids - Equivalent to the sum of all soluble species.

TOS--Total Oxidizable Sulfur - Equivalent to the sum of all sulfite and bisulfite species.

APPENDIX A

LIST OF LABORATORY EXPERIMENTS

LIST OF LABORATORY EXPERIMENTS

Experimental Series	Description	Dates Conducted	Text References
1-10	Sulfuric Acid Treatment, Continuous Reactor	7/73-10/73	V-A
PN1-PN17	Concentrated Lime (Partial Neutralization), Continuous Reactor	10/73-1/74	IV-B
A-H	Concentrated Limestone, Batch Reactions	2/74	VI-A
C1-C32	Concentrated Limestone, Continuous Reactor	3/74-8/74	VI-A
35-45	Concentrated Lime (Effects of TOS on Sulfate Precipitation), Continuous Reactor	9/74-11/77	IV-B
46-65	Dilute Lime Batch and Continuous Reactor Runs	12/74-1/75	VII-A
66-83	Concentrated Limestone, Supplemental Batch and Continuous Reactor Runs	2/75-6/75	VI-B
T1-T30	Proctor Compaction Runs for Studies of Density, Strength, Permeability, Leachability of Treated and Untreated Product Solids	7/75-2/76	VIII

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APPENDIX B

LIST OF PILOT PLANT RUNS

TABLE B-1

LIST OF PILOT PLANT RUNS

Test Series	Mode	Test No.	Type of Operation	Dates Conducted	Test Reference
300	Scrubber Evaluation	301-314	Open-loop, scrubber only	10-11/73	[illegible]
	Sulfuric Acid Treatment	315-320	Closed-loop, integrated system	12/73	[illegible]
		350-357	Open-loop H_2SO_4 reactor	10-11/73, 1/74	[illegible]
100-400	Concentrated Lime/Limestone	101-103	Open-loop, concentrated lime, continuous reactor	1/74	[illegible]
		120-129	Open-loop, concentrated limestone, continuous reactor	7-8/75	[illegible]
		200-212	Open-loop, concentrated lime, batch reactor	2-3/74, 8/74	[illegible]
		301-304	Open-loop, concentrated lime, continuous reactor	3/74	[illegible]
		401-406	Closed-loop, concentrated lime, short-term	4/74, 8/74	[illegible]
		410-412	Closed-loop, concentrated limestone short-term	5/74, 12/75	[illegible]
		420-422	Closed-loop, concentrated lime long-term	10-11/75	[illegible]
		430	Closed-loop, concentrated limestone long-term	1/76	[illegible]
		450-452	Open & closed loop centrifuge testing (concentrated lime & limestone)	4-5/74	[illegible]
		460-471	Open & closed loop filter testing (concentrated lime)	7/74	[illegible]
500-600	Dilute Lime	501-511	Open-loop, continuous reactor	6/74 - 1/75	[illegible]
		590-596	Open-loop, batch reactor	12/74	[illegible]
		601-606	Closed-loop short-term	2/75	[illegible]
		620	Closed-loop long-term	4-5/75	[illegible]

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APPENDIX C

BATCH SETTLING TEST METHODS

APPENDIX C

BATCH SETTLING TESTS--EXPLANATION OF PARAMETERS

In order to assess the dewatering properties of the solids produced in the laboratory and pilot plant tests of various dual alkali regeneration reactor schemes, batch settling tests were performed on the reactor effluent slurries. The batch settling tests simply involved allowing a sample of reactor effluent slurry, initially at uniform concentration, to settle in a graduated cylinder. The settling produced a slurry-supernatant interface (meniscus). The position of the meniscus was recorded as a function of time and the meniscus/time data were then evaluated as described by Fitch[12] to determine settling parameters that would quantify the settling behavior and provide a basis for comparison of the quality of solids produced under the various reactor conditions tested.

The three parameters determined from the batch tests performed in this program were the bulk (initial) settling rate, the maximum solids flux, and the density or insoluble solids content of the settled, partially compacted solids approximately two hours after the completion of the settling test. The bulk settling rate was estimated from plots of the meniscus position versus time. Three different types of settling plots can be employed: log-log (logarithm of meniscus position versus the logarithm of time), semi-log (logarithm of meniscus position versus time), and linear. In any of these plots the curves typically exhibit three characteristic regions--a constant rate section at the beginning of settling, followed by a first falling-rate section (transition zone), and finally a second falling-rate section (compression zone). Figure C-1 shows these three regions in a semi-log plot of settling data taken during the testing of the ADL two-stage reactor in the concentrated lime mode (run 402).

The constant rate section of the plot is frequently referred to as "free settling". During free settling, the rate of meniscus fall is a function of the slurry concentration and the type of solids (density, particle size, and crystalline morphology) and, to a lesser extent, the density of the mother liquor. For a given solids material, say $CaSO_3/CaSO_4$ mixed solids, the free settling behavior will be determined primarily by the particle size distribution and the slurry concentration. The rate of fall during free settling is commonly called the bulk (or initial) settling rate and is a principal parameter in the sizing of clarifiers.

The first falling-rate section is the result of the collapse of solids against the bottom of the column. Solids begin to back up, and the zones of free settling concentrations cannot transmit solids at the rate at which they are settling in from above. The time at which such transition settling occurs and its duration is strongly a function of the quantity of solids in the initial slurry and the rate at which they settle. As shown in Figure C-1, one of the settling curves exhibited essentially no transition zone settling.

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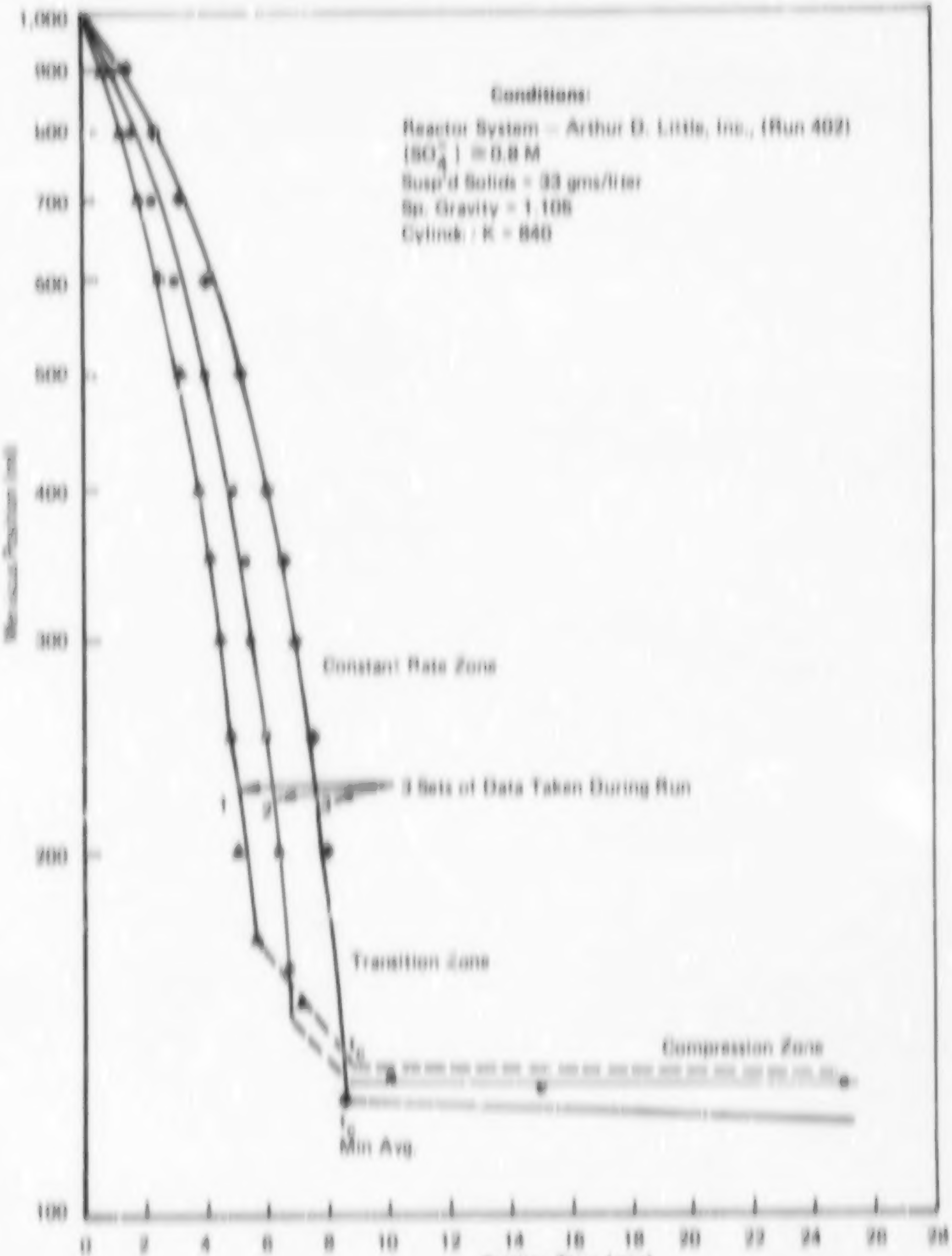

FIGURE C-1 REPRESENTATIVE SETTLING CURVE – CONCENTRATED LIME MODE

The second falling-rate section is the period when solids are compacting at the bottom of the column. The point of discontinuity between the first and second falling-rate sections of the curve is called the "compression point". This is a critical parameter in the determination of the maximum solids flux that can be passed through a thickener. Hence, the compression point is the basis for sizing thickener areas. In a semi-log plot the compression point time is at the intersection of the tangents drawn through the first and second falling-rate sections of the curve.

The maximum solids flux for sizing the thickener is expressed in terms of the compression time as follows:

$$G_t = \frac{45W}{t_u K} , \qquad (C\text{-}1)$$

> where G_t is the flux in tons of solids/(sq. ft.)(day); W is grams of solids in the batch tests; t_u is the "underflow" time; and K is the graduated cylinder constant (cc/ft. of cylinder height). Here, t_u is the time at which the desired underflow concentration is achieved and is related to the compression point time by the following equation:

$$t_u = t_c + \frac{\Theta\ (H_c - H_u)}{2.3\ (H_c - H_\infty)} , \qquad (C\text{-}2)$$

> where t_c is the compression point time in minutes; H_c is the meniscus height at the compression point; H_u is the meniscus height at the desired underflow concentration; H_∞ is the final meniscus height; and Θ is the time interval required for the tangent line constructed to the first falling-rate section to cover one log cycle.

Assuming that the desired underflow concentration is equal to that achieved at the compression point—a reasonable assumption both for designing thickeners as well as comparing the quality of solids from different tests—then the maximum solids flux becomes:

$$G_t = \frac{45W}{t_c K} . \qquad (C\text{-}3)$$

The third parameter, the density of the settled solids, is probably the best measure of the filterability of the solids, since it is an indication of how well the particles compact under the force of gravity. The density of the settled solids is estimated at H_∞ (actually at two hours following the compression point time). The density is calculated using the following equation:

$$\text{Settled Density: } \frac{W}{\left(V_s - \frac{W}{\rho_s}\right)\rho_\ell + W}\,, \qquad \text{(C-4)}$$

where V_s is the volume of the settled solids; and ρ_s and ρ_ℓ are the specific gravities of the solids and liquor, respectively.

Table C-1 lists the values of the three parameters discussed above calculated for the settling curves shown in Figure C-1.

TABLE C-1

SETTLING PARAMETERS FOR CURVES IN FIGURE C-1

Curve	Bulk Settling Rate (ft/min)	Maximum Solids Flux, G_L (tons/ft^2 day)	Density of Settled Solids (wt%)
1	0.21	0.21	22
2	0.26	0.21	22
3	0.12	0.21	25

APPENDIX D

SULFURIC ACID MODEL

APPENDIX D

SULFURIC ACID REACTOR MODEL

A model of the sulfuric acid reactor system was developed to provide a method for estimating reasonable sulfuric acid reactor operating conditions for pilot plant testing, by determining the sulfuric acid requirements in different dual alkali system applications.

The model is based upon the following overall reaction:

$$Na_2SO_4 + H_2SO_4 + 2CaSO_3 \cdot \tfrac{1}{2}H_2O + 3H_2O \rightarrow 2CaSO_4 \cdot 2H_2O + 2NaHSO_3 \qquad \text{(D-1)}$$

Since this reaction proceeds at pH's below 4 (in order to dissolve calcium sulfite), sulfuric acid is also consumed in neutralizing the alkalinity in the cake and acidifying the incoming liquor. These neutralization and acidification reactions are included in the model as follows:

$$Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + CO_2\uparrow \qquad \text{(D-2)}$$

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O \qquad \text{(D-3)}$$

$$2Na_2SO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2NaHSO_3 \qquad \text{(D-4)}$$

$$CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_2\uparrow \qquad \text{(D-5)}$$

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O \qquad \text{(D-6)}$$

All of these usages of sulfuric acid are parasitic in the sense that they do not reduce the sodium sulfate content of the system liquor.

ORIGINAL MODEL

The model is formulated to determine the amount of sulfuric acid required to neutralize all alkalinity value in the slurry feed and adjust the pH into the 2.3-3.3 range. The model assumes that chemical equilibrium is achieved throughout the system. Levels of sulfate and calcium in solution in the reactor effluent are determined from an estimate of the apparent solubility product for gypsum ($K_{sp'} = [Ca^{++}] \times [SO_4^{=}]$ with concentrations in mols per liter). The value of $K_{sp'}$ used is the average of the values calculated from the laboratory data for the range of ionic strengths expected in the pilot plant operations. In this model, $K_{sp'}$ is an input and can be adjusted for any desired ionic strength.

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In order to adjust for pH, it has been simply assumed in the original model that enough sulfuric acid is added to convert up to 20% of the system TOS to H_2SO_3 (depending upon the operating pH). This is a rough estimate based upon laboratory results, and is used because of the lack of accurate estimates of the dissociation constant for sulfurous acid at high ionic strengths. No consideration has been given in this original model to the presence of H_2SO_4. At the pH's in most of the tests performed, the amount of HSO_4^- should be less than 5% of the total S(VI) species.

The model is based upon treatment of settler underflow and scrubber bleed in a system similar to that illustrated in Figure D-1, where code numbers for the various streams and their components are as shown. For example, $x_{18,5}$ would be the sodium sulfate concentration (in molarity) in the liquid fraction of the settler underflow slurry.

The model involves four rather simple relationships shown below. Once all inlet concentrations have been converted to mols per liter of liquid phase, the model solves for all flow rates in liters per hour to keep up with the given oxidation rate producing S mols of "fresh" sulfate per hour. The performance of the sulfuric acid reactor is then defined in terms of the soluble sulfate removed per mol of sulfuric acid used. The original model applies only to the $CaSO_3$-limited regime.

Basic Relationships

Letting S = Oxidation rate of TOS within system in mols/hr.

1. $CaSO_3$ req'd = S + $(H_2SO_4)_{added}$ − (H_2SO_4 for $CaCO_3$ and $Ca(OH)_2$)

   + (Dissolved Ca Out Less Ca from $CaSO_4$ in Settler Underflow)

$$Q_{18}x_{18,12} = S + Q_{24}x_{24,6} - Q_{18}(x_{18,10} + x_{18,10}) + \left(\frac{k_1}{k_2}Q_{25} - Q_{18}x_{18,13}\right)$$

where $k_1 = [Ca^{++}][SO_4^=]$, apparent solubility product

$k_2 = [SO_4^=]_{reactor\ effluent}$

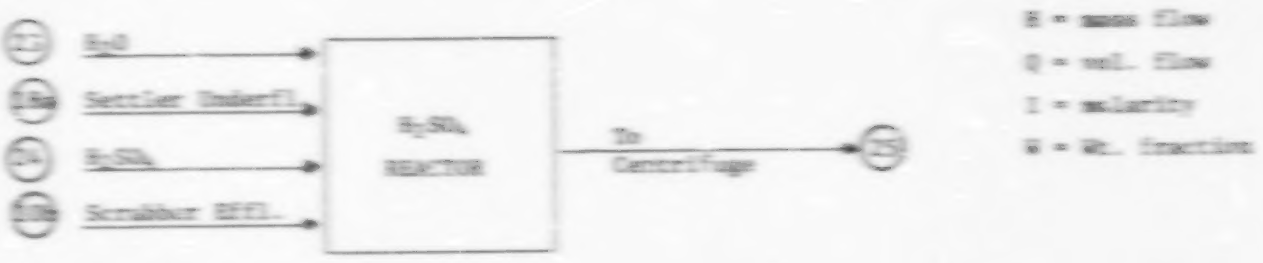
2. H_2SO_4 req'd = (Acid to neutralize OH^-, $SO_3^=$, $CO_3^=$, $CaCO_3$, and $Ca(OH)_2$)

   + (Acid for precipitation of $CaSO_4$)

   + (Acid for pH adjustment)

FIGURE D-1

SCHEMATIC OF H_2SO_4 REACTOR


H_2O
Settler Underfl.
H_2SO_4
Scrubber Effl.
H_2SO_4 REACTOR
To Centrifuge
M = mass flow
Q = vol. flow
I = molarity
W = Wt. fraction

Components:

1 - H_2O
2 - Na_2SO_3
3 - $NaHSO_3$
4 - H_2SO_3
5 - Na_2SO_4
6 - H_2SO_4
7 - NaOH
8 - Na_2CO_3
9 - $NaHCO_3$
10 - $CaCO_3$
11 - $Ca(OH)_2$
12 - $CaSO_3$ - 1/2 H_2O
13 - $CaSO_4$ - 2 H_2O
14 - Impurities in solids (ash, etc.)

$$Q_{24}x_{24,6} = (0.5Q_{18}x_{18,7} + 0.5Q_{18}x_{18,2} + 0.5Q_{19}x_{19,2} + Q_{18}x_{18,8} + Q_{18}x_{18,10} + Q_{18}x_{18,11}) + (0.5Q_{18}x_{18,7} + 0.5Q_{18}x_{18,2} + 0.5Q_{19}x_{19,2} + Q_{18}x_{18,8} + Q_{18}x_{18,5} + Q_{19}x_{19,5}) + k_3(Q_{18}x_{18,2} + Q_{19}x_{19,2} + Q_{19}x_{19,3} + Q_{18}x_{18,3} + Q_{18}x_{18,12})$$

where k_3 = a factor to allow for the formation of H_2SO_3 and the precipitation of the $SO_4^=$ added to get the H_2SO_3.

3. Soluble $SO_4^=$ Feed = S + (Soluble SO_4 effluent in excess of $CaSO_4$ from settler underflow)

$$Q_{18}x_{18,5} + Q_{19}x_{19,5} = S + (k_2Q_{25} - Q_{18}x_{18,15})$$

4. Volume of Liquid Reactor Effluent = (Volume of Settler Underflow)
+ (Volume of Scrubber Effluent)
+ (Volume of Sulfuric Acid)
− (Volume Increase of Solids in Effluent)
− (Apparent Volume Disappearance of H_2O taken up as water of crystallization)

$$Q_{25} = Q_{18} + \frac{F}{1-F}Q_{18} + \frac{k_4}{x_{24,6}} - \frac{172(x_{18,10} + x_{18,11} + x_{18,12} + x_{18,13}) + 60x_{18,14}}{(2.34)(1000)} - \frac{18(x_{18,10} + x_{18,11} + 1.5x_{18,12})}{1000}$$

where $F = Q_{19}/(Q_{18} + Q_{19})$

$$k_4 = Q_{24}x_{24,6}/Q_{18} = x_{18,7} + x_{18,2} + 2x_{18,8} + x_{18,10} + x_{18,5} + x_{18,11} + k_3(x_{18,2} + x_{18,3} + x_{18,12}) + \frac{F}{1-F}\left[x_{19,2} + x_{19,5} + k_3(x_{19,2} + x_{19,3})\right]$$

172 = MW of $CaSO_4 \cdot 2H_2O$
60 = MW of SiO_2 ("impurity")
18 = MW of H_2O
2.34 = Sp. Gr. of mixed $CaSO_4 \cdot 2H_2O$ and of impurity

It can be shown that the above equations all condense to provide the key flow rate for stream 18 (the settler underflow required):

$$Q_{18} = S\,\frac{-k_9 \pm \left(\sqrt{k_9^2 - 4k_8}\right)}{2k_5}$$

where

k_1, k_2, k_3, k_4, F, and S have been defined and

$$k_5 = 1 + \frac{F}{1 - F} + \frac{x_4}{x_{16,6}} - \frac{177\,x_{18,10} + x_{18,12} + x_{18,13} + 60x_{18,14}}{(2.34)(1000)}$$

$$- \frac{18\,x_{18,10} + 1.5x_{18,12}}{1000}$$

$$k_6 = k_4 - x_{18,16} - x_{18,13}$$

$$k_7 = x_{18,5} + x_{18,13} + \frac{F}{1 - F}\,x_{16,5}$$

$$k_8 = k_7x_{18,12} - k_6k_7 - k_1k_5^2$$

$$k_9 = k_6 - k_7 - x_{18,12}$$

Once Q_{18} is known all the other flows follow from the relations under (6) above and the efficiency can be calculated:

$$\text{Efficiency} = \frac{\text{mols } Na_2SO_4 \text{ removed}}{\text{mol } H_2SO_4 \text{ added}}$$

The degree of success of the sulfuric acid treatment system was thus evaluated in terms of the ratio of Na_2SO_4 removed (from that originally present in the scrubber bleed and thickener underflow) to the amount of sulfuric acid fed. Obviously it is desirable that this ratio be as high as possible, realizing that it must be below unity. The model was used to estimate the effects of different process variables on this efficiency ratio. Variables studied included: lime/limestone utilization, solids concentration in the underflow slurry-scrubber bleed composition, and the ratio of scrubber bleed to thickener underflow.

The results of these parametric studies were used as a guide in choosing satisfactory regimes of reactor operation for pilot plant testing. As an example of the use to which it was put, see Figure D-2, in which the effect of high $CaCO_3$ content in the feed solids (low lime/limestone utilization) is shown to be quite severe in limiting H_2SO_4 reactor efficiency. Note that since the liquor composition in this example is the same for both the scrubber effluent and the settler underflow, proceeding to the right is merely equivalent to lowering the percent solids in the underflow, starting from 20% solids at the left and ending with about 11% solids on the right. It is clear in this example that at 20% solids there is already enough Na_2SO_4 in the solution to be equivalent to the $CaCO_3$ present, and that introducing more solution simply increases the volume of reactor effluent, raising the reactor effluent sulfate loss and lowering the efficiency as shown.

MODEL REFINEMENTS

While the original model was quite accurate in the operating regime for which it was designed, it was limited, in that it:

- was restricted to the calcium sulfite-limited regime;
- assumed a split (20%) for H_2SO_3/TOS;
- required an independent estimate and input of the value of the apparent K_{sp}' for gypsum;
- used a simple adjustment factor to account for changes in water of crystalization; and
- did not take into account the formation of HSO_4^-.

A more general model can be developed to overcome these deficiencies. The model would be based upon the neutralization equations of the simplified model, but would utilize the method of Kusik and Meissner[7] to predict the equilibrium composition of the effluent liquor from estimates of appropriate activity coefficients. The activity coefficient estimates would be used to calculate the dissociation constants of sulfurous acid (H_2SO_3), bisulfate (HSO_4^-), and the solubility product of gypsum. Such a model would apply to all modes of operation at pH's ranging from approximately 2.0 to 4.0.

The reaction equations appropriate to the refined model are as follows:

$$CO_3^= + (H_2SO_4) \rightarrow SO_4^= + H_2O + CO_2\uparrow \qquad (D-7)$$

$$2OH^- + (H_2SO_4) \rightarrow SO_4^= + 2H_2O \qquad (D-8)$$

$$2SO_3^= + (H_2SO_4) \rightarrow 2HSO_3^- + SO_4^= \qquad (D-9)$$

$$CaCO_3 + (H_2SO_4) \rightarrow Ca^{++} + SO_4^= + CO_2\uparrow \qquad (D-10)$$

$$Ca(OH)_2 + (H_2SO_4) \rightarrow Ca^{++} + SO_4^= + 2H_2O \qquad (D-11)$$

$$2CaSO_3 \cdot \tfrac{1}{2}H_2O + (H_2SO_4) \rightarrow 2Ca^{++} + 2HSO_3^- + SO_4^= + H_2O \qquad (D-12)$$

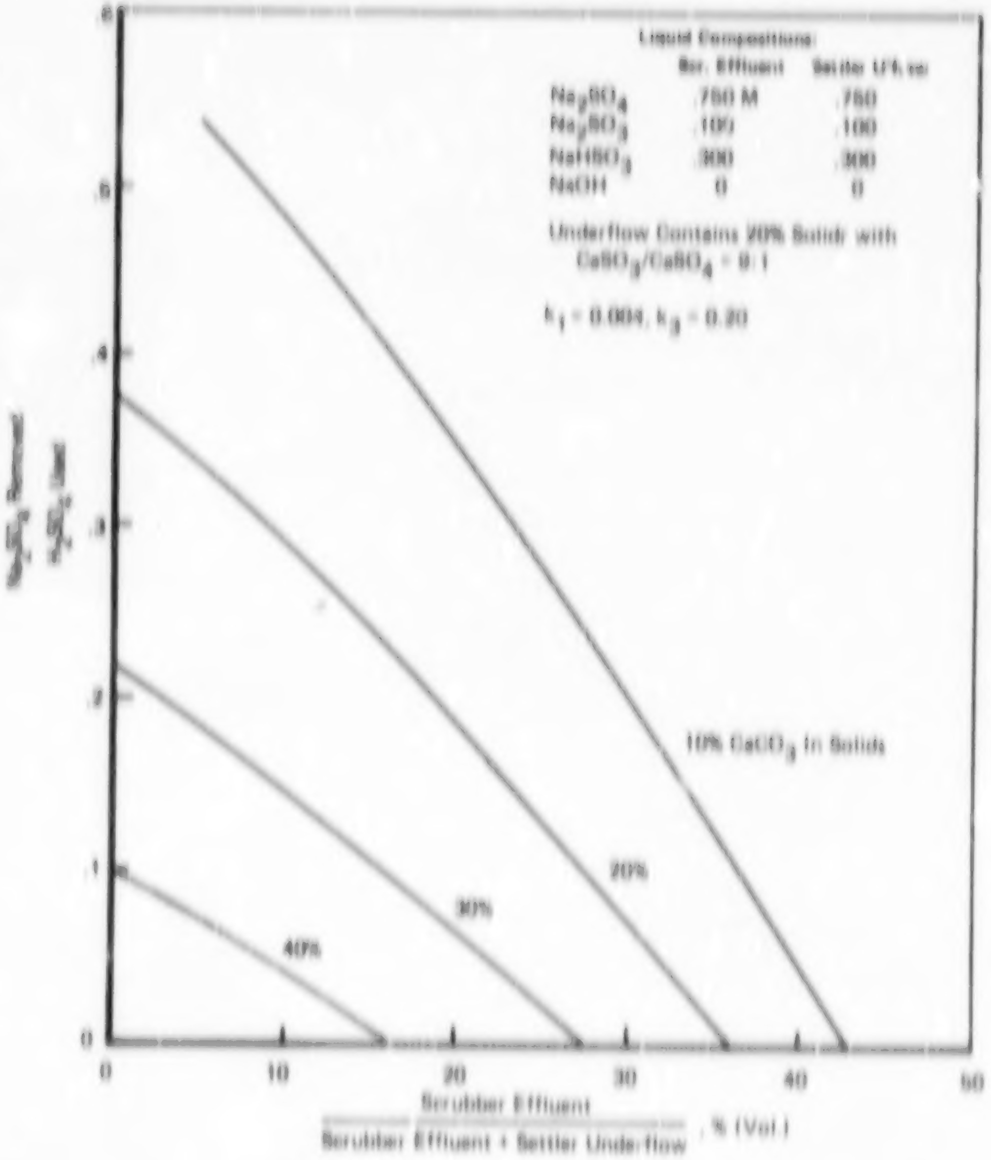


FIGURE D-2 EFFECTS OF LIME/LIMESTONE UTILIZATION AND FEED SOLIDS CONCENTRATION ON THE SULFURIC ACID REACTOR EFFICIENCY

The equilibrium equations governing the composition of the effluent solution would be:

$$\frac{[H^+][HSO_3^-]}{[H_2SO_3]} = K_{H_2SO_3}\ \gamma_{H_2SO_3}\ f_1(\mu)$$

$$\frac{[H^+][SO_4^=]}{[HSO_4^-]} = K_{HSO_4^-}\ f_2(\mu)$$

$$[Ca^{++}][SO_4^=] = K_{CaSO_4}\ f_3(\mu)$$

where, $[H^+] = 10^{-pH}$, and

μ = ionic strength

The success of this simulation is, of course, dependent on the validity of the assumptions and the functional relationships derived for the above equilibrium equations. As a first approximation, it can be assumed that:

- The ionic strength of the liquor will be between 1 and 4.
- The predominant species (dissolved compounds) in solution are Na_2SO_4 and $NaHSO_3$. The reduced activity coefficients of these species are about equal and values for Na_2SO_4 can be used.
- Other ionic species in solution in much lower concentrations are HSO_4^- and $SO_3^=$ and trace value activity coefficients can be used for these electrolyte species.
- The amount of undissociated H_2SO_3 is relatively small and its activity coefficient is approximately 0.1

The equilibrium equations then become:

$$\frac{[H^+][HSO_3^-]}{[H_2SO_3]} = 0.00576\ \mu^{0.31}$$

$$\frac{[H^+][SO_4^=]}{[HSO_4^-]} = 0.047$$

$$[Ca^{++}][SO_4^=] = 0.003e^{0.7\mu} \text{ (for } 1 \le \mu \le 5\text{, based upon laboratory results)}$$

where all concentrations are expressed in mols/liter.

Given the desired pH of operation and the compositions of the feed streams (filter cake or underflow slurry, sulfuric acid and scrubber bleed), these equilibrium equations can be solved in conjunction with the neutralization reaction equations and overall material balances by an iterative procedure to determine the effluent liquor composition and reactor efficiency (with respect to utilization of sulfuric acid). While the model was not programmed for the computer, it was checked against the results of a number of representative runs made in the pilot plant. Table D-1 shows a comparison of pilot plant results with those predicted using both the original and refined models. It has been assumed in using the models that there is no offgassing of SO_2, no oxidation of sulfite, and that all calcium sulfite is dissolved (which has been verified by pilot plant tests).

In general the predicted efficiencies using the original model tended to fall below the observed reactor efficiencies, while those of the refined model tended to exceed the observed efficiencies. In both cases this appears to be due to the inaccuracies in the quantity and composition of the feed solids. Predicted effluent concentrations of TOS based upon the feed liquor composition were consistently higher than observed values. Thus, the models are estimating higher levels of $CaSO_3$ dissolving than actually occurring. With the original model, where the additional acid required to form H_2SO_3 is estimated as a fraction of the total TOS present, this tends to overestimate acid requirements.

For the refined model where estimates of H_2SO_3 are based upon the observed pH, the higher levels of TOS have less of an effect on the acid requirement, but do calculate higher levels of calcium sulfite available to precipitate sulfate (and thereby increase efficiencies). This confirms the results of the variables study which showed that estimates of reactor efficiency are particularly sensitive to the amount of $CaSO_3$ fed to the reactor (in terms of either the level or composition of insoluble solids).

TABLE D-1

COMPARISON OF PILOT PLANT RESULTS WITH ORIGINAL AND REFINED MODELS

FEED RATIO (mole Na_2SO_4/mol $CaSO_3$)	Run No.	EXPERIMENTAL RESULTS Effluent Liquor Composition pH	 $[Ca^{++}]$	 $[SO_4^=]$	 [TDS]	 Efficiency	PREDICTED EFFICIENCIES Refined Model Efficiency	 Original Model
<0.5	056	2.6	0.0098*	0.22*	0.95*	0.22	0.31	-
	055	2.7	0.015	0.13	1.05	0.37	0.42	-
>0.5	050	2.9	0.017	0.17	0.75	0.43	0.51	0.45
	051	2.8	0.014	0.29	0.59	0.28	0.45	0.19
	054	2.3	0.008	0.60	0.60	-0.01	0.12	<0